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ANTIREFLECTIVE HARDMASK
COMPOSITIONS AND USES THEREOF

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SUBMISSION UNDER 37 CFR 1.99

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Sir:

Please enter this submission in the file of the above application. The following references are being submitted for consideration by the Patent Office:

1. U.S. Patent No. 6,420,088 B1 to Angelopoulos et al., issued on July 16, 2002, from U.S. Patent Application No. 09/602,967, filed June 23, 2000;

2. U.S. Patent No. 6,730,454 B2 to Pfeiffer et al., issued on May 4, 2004, from U.S. Patent Application No. 10/124,087, filed April 16, 2002; and

3. U.S. Patent Application Publication No. 2004/0229158 A1 to Meador et al., published on November 18, 2004, from U.S. Patent Application No. 10/784,045, filed February 20, 2004.

A check for the sum of $180.00 is enclosed to cover the submission fee under 37 CFR 1.17(p).

The undersigned certifies that a copy of this submission has been sent by postage prepaid first class mail to Ryan, Mason & Lewis, LLP, 1300 Post Road, Suite 205, Fairfield, CT 06824.

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(54) LITHOGRAPHIC ANTIREFLECTIVE HARDMASK COMPOSITIONS AND USES THEREOF

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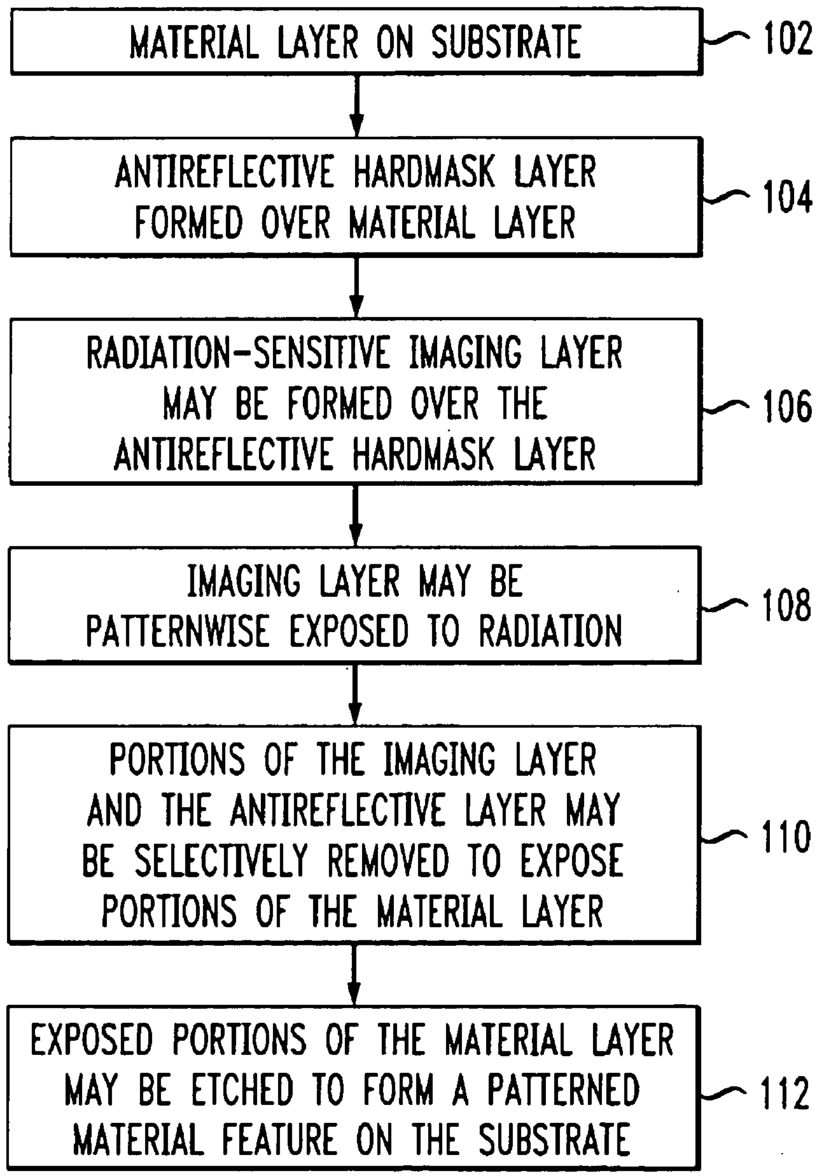
(57) **ABSTRACT**

Compositions and techniques for the processing of semiconductor devices are provided. In one aspect of the invention, an antireflective hardmask composition is provided. The composition comprises a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8; and at least one chromophore moiety and transparent moiety. In another aspect of the invention, a method for processing a semiconductor device is provided. The method comprises the steps of: providing a material layer on a substrate; forming an antireflective hardmask layer over the material layer. The antireflective hardmask layer comprises a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8; and at least one chromophore moiety and transparent moiety.

FIG. 1


MATERIAL LAYER ON SUBSTRATE
102
ANTIREFLECTIVE HARDMASK LAYER FORMED OVER MATERIAL LAYER
104
RADIATION-SENSITIVE IMAGING LAYER MAY BE FORMED OVER THE ANTIREFLECTIVE HARDMASK LAYER
106
IMAGING LAYER MAY BE PATTERNWISE EXPOSED TO RADIATION
108
PORTIONS OF THE IMAGING LAYER AND THE ANTIREFLECTIVE LAYER MAY BE SELECTIVELY REMOVED TO EXPOSE PORTIONS OF THE MATERIAL LAYER
110
EXPOSED PORTIONS OF THE MATERIAL LAYER MAY BE ETCHED TO FORM A PATTERNED MATERIAL FEATURE ON THE SUBSTRATE
112

LITHOGRAPHIC ANTIREFLECTIVE HARDMASK COMPOSITIONS AND USES THEREOF

FIELD OF THE INVENTION

[0001] The present invention relates to semiconductor devices and, more particularly, to the processing of semiconductor devices.

BACKGROUND OF THE INVENTION

[0002] In the microelectronics industry, as well as in other industries involving construction of microscopic structures, e.g., micromachines and magnetoresistive heads, there is a desire to further reduce the size of structural features. In the microelectronics industry in particular, while the size of microelectronic devices is being reduced, a greater amount of circuitry for a given chip size is being required.

[0003] Effective lithographic techniques are essential to reducing the size of structural features. Lithography impacts the manufacture of microscopic structures, not only in terms of directly imaging patterns on the desired substrate, but also in terms of making masks typically used in such imaging.

[0004] Most lithographic processes use an antireflective coating (ARC) to minimize the reflectivity between an imaging layer, such as a radiation-sensitive resist material layer, and an underlayer to enhance resolution. However, these ARC materials impart poor etch selectivity to the imaging layer due to the layers' similar elemental compositions. Therefore, during etching of the ARC after patterning, a lot of the imaging layer is also consumed, which may have been needed for additional patterning during subsequent etch steps.

[0005] In addition, for some lithographic techniques, the radiation-sensitive resist material employed does not provide resistance to subsequent etching steps sufficient enough to enable effective transfer of the desired pattern to the layer underlying the radiation-sensitive resist material. In many instances, a hardmask layer is used, for example, where an ultrathin radiation-sensitive resist material is used, where the underlying layer to be etched is thick, where a substantial etching depth is required, where it is desirable to use certain etchants for a given underlying layer, or any combination of the above. The hardmask layer serves as an intermediate layer between the patterned radiation-sensitive resist material and the underlying layer to be patterned. The hardmask layer receives the pattern from the patterned radiation-sensitive resist material layer and transfers the pattern to the underlying layer. The hardmask layer should be able to withstand the etching processes required to transfer the pattern.

[0006] While many materials useful as ARC compositions are known, there is a need for improved ARC compositions with high etch selectivity to the radiation-sensitive resist material, to the hardmask layer and to the underlying layer. Further, many of the known ARCs are difficult to apply to the substrate, e.g., applying these ARCs may require the use of chemical vapor deposition, physical vapor deposition, special solvents, high temperature baking or any combination of the above.

[0007] It would be desirable to perform lithographic techniques with a high etch selectivity and a sufficient resistance to multiple etchings. These lithographic techniques would enable production of highly detailed semiconductor devices.

SUMMARY OF THE INVENTION

[0008] The present invention provides compositions and techniques for the processing of semiconductor devices. In one aspect of the invention, an antireflective hardmask composition is provided. The composition comprises a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8; and an equivalent number of at least one chromophore moiety and transparent moiety. The composition may comprise any combination of an acid generator, a crosslinking component and an additional crosslinking component.

[0009] In another aspect of the invention, a method for processing a semiconductor device is provided. The method comprises the steps of: providing a material layer on a substrate; and forming an antireflective hardmask layer over the material layer. The antireflective hardmask layer comprises a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8; and at least one chromophore moiety and transparent moiety. The method may further comprise the steps of: forming a radiation-sensitive imaging layer over the antireflective layer; patternwise exposing the radiation-sensitive imaging layer to radiation thereby creating a pattern of radiation-exposed regions in the imaging layer; selectively removing portions of the radiation-sensitive imaging layer and the antireflective hardmask layer to expose portions of the material layer; and etching the exposed portions of the material layer, thereby forming a patterned material feature on the substrate.

[0010] A more complete understanding of the present invention, as well as further features and advantages of the present invention, will be obtained by reference to the following detailed description and drawing.

BRIEF DESCRIPTION OF THE DRAWING

[0011] **FIG. 1** is a flow chart illustrating an exemplary technique for processing a semiconductor device according to an embodiment of the present invention.

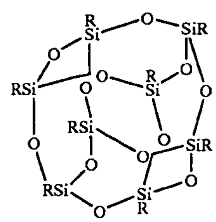
DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0012] An antireflective hardmask composition (hereinafter "the composition") is disclosed herein. The composition comprises a fully condensed polyhedral oligosilsesquioxane (POSS) material. The fully condensed POSS material may comprise the units $\{RSiO_{1.5}\}_n$, wherein n equals 6 to 12.

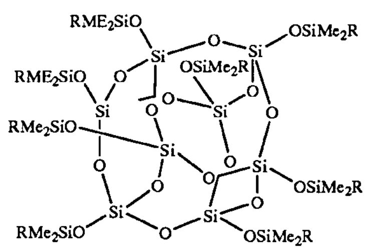
[0013] In an exemplary embodiment, the fully condensed POSS material is selected from a cubic moiety of the formula $\{RSiO_{1.5}\}_n$, wherein n equals 8 and comprising SiO bonds. This fully condensed POSS material should have solution and film-forming characteristics conducive to forming a layer by conventional spin-coating.

[0014] The fully condensed POSS material may have either of General Structures I and II shown below:

I



II



[0015] wherein R comprises a chromophore moiety and/or a transparent moiety. The R group may further serve as a crosslinking component. The R group can crosslinking component with or without an additional crosslinking component depending on the chemical nature of the R group. An additional crosslinking component is described below. In some instances, multiple functional moieties may be present on the same POSS unit. Thus, for example, a chromophore moiety and a transparent moiety may be present on the same POSS unit. It may be desirable to blend POSS units containing a chromophore moiety, a transparent moiety and/or a crosslinking component.

[0016] Generally, all fully condensed POSS materials are suitable for antireflective hardmask applications since the absence or minimum inclusion of SiOH groups enhances the stability of the POSS material for storage. However, General Structures I and II, shown above, are preferred. As shown in General Structure II, the POSS material may comprise $OSiMe_2$ units on each corner of the cubic moiety.

[0017] The antireflective hardmask composition of the present invention may comprise, on a solids basis, from about 50 weight percent (wt. %) to about 98 wt. % POSS material. For example, the composition may comprise, on a solids basis, from about 70 wt. % to about 80 wt. % POSS material.

[0018] Suitable chromophore moieties include those chromophore moieties which can be grafted onto an SiO moiety of the POSS material, have suitable radiation absorption characteristics and do not adversely affect the performance of the antireflective hardmask composition, or any overlying radiation-sensitive layers, as will be described in detail below. Suitable chromophore moieties include, but are not limited to, phenyl, chrysenes, pyrenes, fluoranthrenes, anthrones, benzophenones, thioxanthones, and anthracenes. Anthracene derivatives, such as those described in Renner, U.S. Pat. No. 4,371,605, "Photopolymerizable Compositions Containing N-hydroxyamide and N-hydroxyimide Sulfonates," the disclosure of which is incorporated by reference herein, may also be used. 9-Anthracene methanol is a preferred chromophore for 248 nanometer (nm) applications. The chromophore moiety preferably does not contain nitrogen, except for possibly deactivated amino nitrogen such as in phenol thiazine. For 193 nm radiation, non-aromatic compounds containing unsaturated carbon bonds, e.g., carbon to carbon double bonds, are also suitable chromophores. For 157 nm radiation, compounds containing saturated carbon to carbon bonds can act as chromophores.

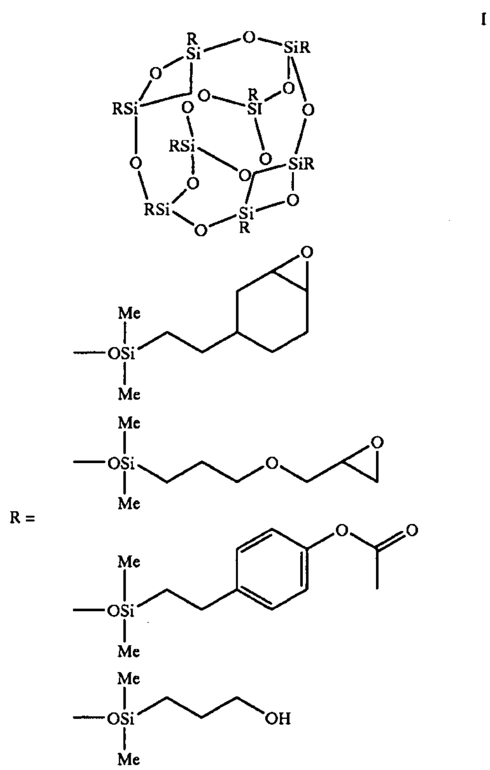
[0019] The chromophore moieties may be chemically attached to the SiO component of a POSS unit by acid-catalyzed O-alkylation or acid-catalyzed C-alkylation, such as by Friedel-Crafts alkylation. Alternatively, the chromophore moiety may be attached to a POSS unit by an esterification mechanism. In an exemplary embodiment, from about five percent to about 40 percent of the POSS units contain chromophore moieties. The sites for attachment of the chromophore moieties may be an aromatic group such as a hydroxybenzyl or hydroxymethylbenzyl group. Alternatively, the chromophore moieties may be attached to a POSS unit by reaction with other moieties such as cyclohexanol or another alcohol. The reaction used to attach the chromophore moieties may comprise an esterification of an alcohol (OH) group.

[0020] Suitable transparent moieties may vary depending on the wavelength or character of the imaging radiation. In the cases of 193 or 157 nm imaging radiation, the transparent moieties preferably comprise hydrogen and/or organic groups (C_1 or higher), substantially free of unsaturated carbon to carbon bonds. For example, a suitable transparent moiety for 193 nmi applications is an alcohol or an epoxide. In the case of 157 nm imaging radiation, transparent moieties containing fluorine may be desirable. The amount of transparent moieties is preferably balanced with the amount of chromophore to provide a desired combination of energy absorption and antireflection. Thus in an exemplary embodiment, the composition comprises an equivalent number of chromophore moieties and transparent moieties.

[0021] As mentioned above, the R group can function as a crosslinking component. The crosslinking component can crosslink POSS units in a reaction catalyzed by a generated acid and/or by heating. The R group can function as a crosslinking component with or without an additional crosslinking component. Suitable R group crosslinking components include, but are not limited to, epoxides or alcohols, such as, aromatic alcohols, including, hydroxybenzyl, phenol, hydroxymethylbenzyl or cycloaliphatic alcohols, including, cyclohexanoyl. Alternatively, non-cyclic alcohols, such as fluorocarbon alcohols, aliphatic alcohols, amino groups, vinyl ethers may be employed.

[0022] Generally the chromophore moiety, transparent moiety and/or crosslinking component can be attached to the SiO unit of the POSS material by a hydrosilation reaction or by choosing appropriately functionalized precursors ($RSiOR_3$ or $RSiCl_3$) before the POSS synthesis. See F. J. Feher, *Polyhedral Oligosilsesquioxanes and Heterosilsesquioxanes*, Gelest Catalog, 43-59 (1998), the disclosure of which is incorporated by reference herein.

[0023] Examples of suitable POSS materials with R groups functioning as crosslinking components include those shown in the scheme below:



[0024] The antireflective hardmask composition of the present invention may comprise, on a solids basis, less than or equal to about 50 wt. % crosslinking component. For example, the composition may comprise, on a solids basis, from about five wt. % to about 25 wt. % crosslinking component.

[0025] The composition may further comprise an additional crosslinking component that can be reacted with a POSS unit in a reaction catalyzed by a generated acid and/or by heating. Generally, the additional crosslinking component used in the composition may be any suitable crosslinking agent known in the negative photoresist art which is otherwise compatible with the other selected components of the composition. The additional crosslinking component acts to crosslink POSS units in the presence of a generated acid. Additional crosslinking components include, but are not limited to, glycoluril compounds, such as, tetramethoxymethyl glycoluril, methylpropyltetramethoxymethyl glycoluril and methylphenyltetramethoxymethyl glycoluril, available under the POWDERLINK trademark ftom Cytec Industries, 2,6-bis(hydroxymethyl)-p-cresol compounds such as those found in Masaaki, Japanese Patent Application JP1293339A2, "Photoresist Compositions," the disclosure of which is incorporated by reference herein, etherified amino resins, for example, methylated melamine resins or butylated melamine resins (N-methoxymethyl-melamine or N-butoxymethyl-melamine), methylated glycolurils and butylated glycolurils, for example as can be found in Kirchmayr, Canadian Patent 1204547, "Curable Composition Based On an Acid-Curable Resin, and Process for Curing this Resin," the disclosure of which is incorporated by reference herein. Other crosslinking agents such as bis-epoxies or bis-phenols, e.g., bisphenol-A, may also be used. Combinations of crosslinking agents may be used. In some cases, e.g., where the reactive group is an epoxide, additional crosslinkers may not be necessary.

[0026] In some cases crosslinking can be achieved by irradiation of the material with electron beam irradiation (hereinafter "e-beam"). In these cases, the addition of an additional crosslinking component and an acid generator and/or heating are optional.

[0027] Suitable acid generators include acid generating compounds that liberate acid upon thermal treatment, e.g., thermal acid generators. A variety of known thermal acid generators may be employed, such as, 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate and other alkyl esters of organic sulfonic acids. Compounds that generate a sulfonic acid upon activation are generally suitable. Other suitable thermally activated acid generators are described in Sinta et al., U.S. Pat. No. 5,886,102, "Antireflective Coating Compositions" (hereinafter "Sinta") and in Pavelchek et al., U.S. Pat. No. 5,939,236, "Antireflective Coating Compositions Comprising Photoacid Generators," (hereinafter "Pavelchek"), the disclosures of which are incorporated by reference herein. If desired, a radiation-sensitive acid generator may be employed as an alternative to, or in combination with, a thermal acid generator. Examples of suitable radiation-sensitive acid generators are described in Sinta and Pavelchek. Other radiation-sensitive acid generators known in the resist art may also be used as long as they are compatible with the other components of the composition. Where a radiation-sensitive acid generator is used, the cure, e.g., crosslinking, temperature of the composition may be reduced by the application of appropriate radiation to induce acid generation which in turn catalyzes the crosslinking reaction. Even if a radiation-sensitive acid generator is used, it is preferable to thermally treat the composition to accelerate the crosslinking process, for example, in the case of production line fabrication.

[0028] The antireflective hardmask composition of the present invention may comprise, on a solids basis, from about one wt. % to about 20 wt. % acid generator. For example, the composition may comprise, on a solids basis, from about one wt. % to about 15 wt. % acid generator.

[0029] The composition may be used in combination with any desired resist material to form a lithographic structure. Preferably, the resist is imageable with shorter wavelength ultraviolet radiation, e.g., less than 200 nm wavelength, or with e-beam radiation. Examples of suitable resist materials are described in Bucchignano et al., U.S. Pat. No. 6,037,097, "E-beam Application to Mask Making Using New Improved KRS Resist System," the disclosure of which is incorporated by reference herein.

[0030] The composition will typically contain a solvent prior to application to the desired substrate. The solvent may be any solvent conventionally used with resists which otherwise does not have any excessively adverse impact on the antireflective hardmask performance of the composition. Suitable solvents include, but are not limited to, propylene

glycol monomethyl ether acetate, cyclohexanone and ethyl lactate. The amount of solvent in the composition for application to a substrate should be sufficient to achieve a solids content of about five wt. % to about 20 wt. %. Higher solids content formulations will generally yield thicker coating layers. The composition may further contain minor amounts of auxiliary components, e.g., base additives, as may be known in the art.

[0031] The composition can be prepared by combining the POSS material, crosslinking component and acid generator and any other desired ingredients using conventional methods. The formation of an antireflective hardmask layer using the composition is described below.

[0032] The antireflective hardmask layers are useful for lithographic processes used in the manufacture of integrated circuits on semiconductor substrates. For example, the antireflective hardmask layers are especially useful for lithographic processes using 248 nm, 193 nm, 157 nm, x-ray, e-beam or other imaging radiation. Thus, further disclosed herein is a method for processing a semiconductor device, as shown in **FIG. 1**.

[0033] Semiconductor lithographic applications generally involve transfer of a pattern to a material layer on the semiconductor substrate, as shown in step **102** of **FIG. 1**. The material layer may be a metal conductor layer, a ceramic insulator layer, a semiconductor layer or other material layer depending on the stage of the manufacture process and the desired material set for the end product. The composition may be formed into an antireflective hardmask layer and applied directly over the material layer to be patterned, preferably by spin-coating, as shown in step **104** of **FIG. 1**. The composition is then baked to remove the solvent and to cure, e.g., crosslink, the composition.

[0034] The composition may be formed into antireflective hardmask layers on a substrate by spin-coating followed by baking to achieve crosslinking and solvent removal. The baking is conducted at about 250 degrees centigrade (° C.) or less. For example, baking is conducted at a temperature of from about 150° C. to about 220° C. The baking time may be varied depending on the layer thickness and baking temperature.

[0035] The thickness of the antireflective hardmask layer may vary depending on the desired function. For typical applications, the thickness of the antireflective hardmask layer is from about 0.03 micrometers (μm) to about 5.0 μm.

[0036] If desired, the composition may also be used as a dielectric material in a similar manner to conventional spin-on glass materials. The antireflective hardmask layer resists lateral etch acting as a hardmask even at thin film thickness traditionally associated with organic antireflective layers.

[0037] A radiation-sensitive imaging layer can then be applied, either directly or indirectly, over the cured composition, as shown in step **106** of **FIG. 1**. The radiation-sensitive imaging layer may be applied using spin-coating techniques. The substrate with the material layer, the antireflective hardmask layer and the radiation-sensitive imaging layer may then be heated, e.g., pre-exposure baked, to remove the solvent and improve the coherence of the radiation-sensitive imaging layer. The radiation-sensitive imaging layer should be as thin as possible while still being substantially uniform and sufficient to withstand subsequent processing, such as reactive ion etching, to transfer the lithographic pattern to the underlying substrate material layer. The pre-exposure bake step is preferably conducted for about ten seconds to about 900 seconds. For example, the duration of the pre-exposure bake may be from about 15 seconds to about 60 seconds. The pre-exposure bake temperature may vary depending on the glass transition temperature of the radiation-sensitive imaging layer.

[0038] After solvent removal, the radiation-sensitive imaging layer is then patternwise-exposed to the desired radiation, e.g., 193 nm ultraviolet radiation, as shown in step **108** of **FIG. 1**. Where scanning particle beams, such as an electron beam, are used, patternwise exposure may be achieved by scanning the beam across the substrate and selectively applying the beam in the desired pattern. More typically, where wavelike radiation in used, such as 193 m ultraviolet radiation, the patternwise exposure is conducted through a mask which is placed over the radiation-sensitive imaging layer. For 193 nm UV radiation, the total exposure energy is less than or equal to about 100 millijoules per square centimeter (millijQules/cm^2). For example, the exposure energy may be less than or equal to about 50 millijoules/cm^2. Further, the exposure energy may be from about 15 millijoules/cm^2 to about 30 millijoules/cm^2.

[0039] After the desired patternwise exposure, the radiation-sensitive imaging layer is typically baked, i.e., post-exposure baked, to further complete the acid-catalyzed reaction and to enhance the contrast of the exposed pattern. The post-exposure bake is conducted at a temperature of from about 60° C. to about 175° C. For example, the post-exposure bake is conducted at a temperature of from about 90° C. to about 160° C. The post-exposure bake is conducted for a duration of from about 30 seconds to about 300 seconds.

[0040] After post-exposure bake, the radiation-sensitive imaging layer with the desired pattern is obtained, e.g., developed, by contacting the radiation-sensitive imaging layer with an alkaline solution which selectively dissolves the areas of the radiation-sensitive imaging layer which were exposed to the radiation, as shown in step **110** of **FIG. 1**. Preferred alkaline solutions, e.g., developers, include aqueous solutions of tetramethyl ammonium hydroxide. The resulting lithographic structure on the substrate is then typically dried to remove any remaining developer solvent.

[0041] The pattern from the radiation-sensitive imaging layer may then be transferred to the exposed portions of the antireflective hardmask layer by etching with tetrafluoromethoane (CF_4), or other suitable etchant, using known techniques. The portions of the antireflective hardmask layer may then be removed, as shown in step **110** of **FIG. 1**.

[0042] The exposed underlying material layer to be patterned may then be etched, as shown in step **112** of **FIG. 1**, using an etchant appropriate to that material. For example, when the material layer comprises a metal, such as chromium (Cr), a chlorine/oxygen combination (Cl_2/O_2) may be used as a dry etchant.

[0043] Once the pattern transfer has taken place, any remaining radiation-sensitive imaging layer and antireflective hardmask layer may be removed using conventional stripping techniques. If the antireflective hardmask layer is

being used strictly as a hardmask layer, the composition may be removed using a tetrafluoromethane/oxygen (CF_4/O_2) plasma.

[0044] Thus, the composition and resulting lithographic structures can be used to create patterned material layer structures such as metal wiring lines, holes for contacts or vias, insulation sections, such as, damascene trenches or shallow trench isolation, trenches for capacitor structures, such as those that might be used in the design of integrated circuit devices. The compositions are especially useful in the context of creating patterned layers of oxides, nitrides, polysilicon, and/or chrome.

[0045] Examples of general lithographic processes wherein the composition of the present invention may be useful are disclosed in Douglas, U.S. Pat. No. 4,855,017, "Trench Etch Process for a Single-Wafer RIE Dry Etch Reactor," Bronner et al., U.S. Pat. No. 5,362,663, "Method of Forming Double Well Substrate Plate Trench DRAM Cell Array," Akiba et al., U.S. Pat. No. 5,429,710, "Dry Etching Method," Nulty, U.S. Pat. No. 5,562,801, "Method of Etching an Oxide Layer," Golden et al., U.S. Pat. No. 5,618,751, "Method of Making Single-Step Trenches Using Resist Fill Recess," Chan et al., U.S. Pat. No. 5,744,376, "Method of Manufacturing Copper Interconnect With Top Barrier Layer," Yew et al., U.S. Pat. No. 5,801,094, "Dual Damascene Process," Shanmugham, U.S. Pat. No. 5,821,469, "Device for Securing Cables in a Telecommunications System," Kornblit, U.S. Pat. No. 5,948,570, "Process for Dry Lithographic Etching," the disclosures of which are incorporated by reference herein. Other examples of pattern transfer processes are described in W. MOREAU, SEMICONDUCTOR LITHOGRAPHY, PRINCIPLES, PRACTICES, AND MATERIALS, ch. 12-13 (1988), the disclosure of which is incorporated by reference herein. While exemplary lithographic processes are described and referenced herein, it should be understood that the present invention should not limited to any particular lithographic technique or device structure.

[0046] Further disclosed herein is a patterned lithographic structure. The patterned lithographic structure comprises: a substrate; a material layer over the substrate; a patterned antireflective hardmask layer over the material layer, the patterned antireflective hardmask layer comprising the composition; and a patterned radiation-sensitive imaging layer over the antireflective hardmask layer.

[0047] Although illustrative embodiments of the present invention have been described herein, it is to be understood that the invention is not limited to those precise embodiments, and that various other changes and modifications may be made by one skilled in the art without departing from the scope or spirit of the invention. The following examples are provided to illustrate the scope and spirit of the present invention. Because these examples are given for illustrative purposes only, the invention embodied therein should not be limited thereto.

EXAMPLES

Example 1

[0048] The POSS materials Octakis {(glycidoxypropyl)dimethylsiloxy}silsesquioxane, Octakis {(ethylcyclohexylpropyl)dimethylsiloxy}silsesquioxane, Octakis {(propanol)dimethylsiloxy}silsesquioxane and Octakis {(ethylphenylacetate)dimethylsiloxy}silsesquioxane were obtained from TAL Materials, Inc.

Example 2

[0049] Formulation

[0050] The desired POSS material from Example 1 was dissolved in propylene glycol monomethyl ether acetate (PGMEA) or ethyl lactate in concentrations of 12 percent by weight to the solvent to 14 percent by weight to the solvent. A crosslinking agent tetramethoxymethyl glycoluril, available from DayChem, in a concentration of eight parts by weight relative to POSS and di(t-butylphenyl)iodoniumperfluorobutylsulfonate (DtBPI-PFBuS) in a concentration of four parts by weight relative to POSS were added to the solution.

Example 3

[0051] Film Formation and Optical Properties

[0052] Formulations POSS A, POSS B, POSS C and POSS D comprising Octakis {(glycidoxypropyl)dimethylsiloxy}silsesquioxane, Octakis {(ethylcyclohexylpropyl)dimethylsiloxy}silsesquioxane, Octakis {(propanol)dimethylsiloxy}silsesquioxane and Octakis {(ethylphenylacetate)dimethylsiloxy}silsesquioxane, respectively, prepared as described in Example 2, were spin coated onto a 200 millimeter silicon wafer at 3,000 revolutions per minute for 60 seconds. The film thicknesses ranged from 1,700 to 2,500 angstroms. The spin cast film was cured at 200° C. for 60 seconds. The optical constants, the index of refraction n and the extinction coefficient k at 193 nm, were measured using an n&k Analyzer manufactured by n&k Technology, Inc.

[0053] The optical properties of the films for 193 nm radiation were as follows:

Film POSS	n	K
POSS A	1.611	0.030
POSS B	1.645	0.050
POSS C	1.647	0.026
POSS D	1.689	0.205
POSS A & D (4:1 wt/wt)	1.735	0.278
POSS B & D (4:1 wt/wt)	1.762	0.308

Example 4

[0054] 193 nm Lithography and Etching the Antireflective Hardmask Layer:

[0055] The hardmask layer was formed as described in Example 3 using the mixture of POSS A and POSS D. A layer of PAR 715 acrylic-based photoresist (obtained from Sumitomo) was spin-coated over the cured antireflective hardmask layer to a thickness of about 300 nm. The photoresist was baked at 130° C. for 60 seconds. The photoresist layer was then imaged using a 0.6 NA 193 nm Nikon Stepper with conventional and annular illumination using APSM reticle. After patternwise exposure, the photoresist layer was

baked at 130° C. for 60 seconds. The image was then developed using commercial developer (0.26M TMAH). The resulting pattern showed 113.75 nm and 122.5 nm equal lines and space patterns.

[0056] The pattern was then transferred into the antireflective hardmask layer by a 20 second fluorocarbon based etch using a TEL DRM tool. The etch selectivity between the photoresist and the antireflective hardmask layer exceeded ten to one, demonstrating that virtually no photoresist is lost during the antireflective hardmask open etch.

[0057] The etch selectivity between the films present between the antireflective hardmask layer and an oxide containing material layer was determined on the polymer films from Example 3 to be 2.5 to one and 3.3 to one for the photoresist (PAR 715), respectively, using a fluorocarbon based etch performed on a TEL DRM tool. The combined etch selectivities give an overall etch selectivity of the pattern transfer from oxide to organic photoresist greater than 20 to one which is superior to any known organic hardmasks.

What is claimed is:

1. An antireflective hardmask composition comprising:

a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8; and

at least one chromophore moiety and transparent moiety.

2. The composition of claim 1, comprising from about 50 wt. % to about 98 wt. %, on a solids basis, polyhedral oligosilsesquioxane.

3. The composition of claim 1, comprising from about 70 wt. % to about 80 wt. %, on a solids basis, polyhedral oligosilsesquioxane.

4. The composition of claim 1, wherein each chromophore moiety is selected from the group consisting of phenyl, chrysenes, pyrenes, fluoranthrenes, anthrones, benzophenones, thioxanthones, anthracenes, anthracene derivatives, 9-anthracene methanol, phenol thiazine, non-aromatic compounds containing unsaturated carbon to carbon double bonds, compounds containing saturated carbon to carbon bonds and compositions comprising at least one of the foregoing chromophores.

5. The composition of claim 1, wherein each transparent moiety is substantially free of unsaturated carbon to carbon double bonds.

6. The composition of claim 1, wherein at least one transparent moiety comprises fluorine.

7. The composition of claim 1, wherein less than or equal to about 50 percent of the transparent moieties present are free of unsaturated carbon to carbon bonds.

8. The composition of claim 1, wherein each transparent moiety is transparent to 157 nanometer radiation.

9. The composition of claim 1, comprising an equivalent number of chromophore and transparent moieties.

10. The composition of claim 1, further comprising a crosslinking component.

11. The composition of claim 10, wherein the crosslinking component is selected from the group consisting of epoxides, alcohols, aromatic alcohols, hydroxybenzyl, phenol, hydroxymethylbenzyl, cycloaliphatic alcohols, cyclohexanoyl, non-cyclic alcohols, fluorocarbon alcohols, aliphatic alcohols, amino groups, vinyl ethers and compositions comprising at least one of the foregoing crosslinking components.

12. The composition of claim 10, comprising less than or equal to about 50 wt. %, on a solids basis, crosslinking component.

13. The composition of claim 10, comprising from about five wt. % to about 25 wt. %, on a solids basis, crosslinking component.

14. The composition of claim 1, further comprising an additional crosslinking component.

15. The composition of claim 14, wherein the additional crosslinking component is selected from the group consisting of glycoluril, methylated glycoluril, butylated glycoluril, tetramethoxymethyl glycoluril, methylpropyltetramethoxymethyl glycoluril, methylphenyltetramethoxymethyl glycoluril, 2,6-bis(hydroxymethyl)-p-cresol, etherified amino resins, methylated melamine resins, N-methoxymethyl-melamine, butylated melamine resins, N-butoxymethyl-melamine, bis-epoxies, bis-phenols, bisphenol-A, and compositions comprising at least one of the foregoing crosslinking components.

16. The composition of claim 1, further comprising an acid generator.

17. The composition of claim 16, wherein the acid generator is selected from the group consisting of 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate, alkyl esters of organic sulfonic acids, and combinations comprising at least one of the foregoing acid generators.

18. The composition of claim 16, wherein the acid generator is a thermal acid generator.

19. The composition of claim 16, comprising from about one wt. % to about 20 wt. %, on a solids basis, acid generator.

20. The composition of claim 16, comprising from about one wt. % to about 15 wt. %, on a solids basis, acid generator.

21. A method for processing a semiconductor device, the method comprising the steps of:

providing a material layer on a substrate;

forming an antireflective hardmask layer over the material layer, the antireflective hardmask layer comprising:

a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8; and

at least one chromophore moiety and transparent moiety.

22. The method of claim 21, further comprising the steps of:

forming a radiation-sensitive imaging layer over the antireflective hardmask layer;

patternwise exposing the radiation-sensitive imaging layer to radiation thereby creating a pattern of radiation-exposed regions in the imaging layer;

selectively removing portions of the radiation-sensitive imaging layer and the antireflective hardmask layer to expose portions of the material layer; and

etching the exposed portions of the material layer, thereby forming a patterned material feature on the substrate.

23. The method of claim 22, further comprising the step of removing remaining radiation-sensitive imaging layer and antireflective hardmask layer from the material layer.

24. The method of claim 22, wherein the radiation is ultraviolet radiation having a wavelength of less than or equal to about 200 nanometers.

25. The method of claim 22, wherein the radiation is electron beam radiation.

26. The method of claim 21, wherein the material layer comprises a material selected from the group consisting of a conductive material, a semiconductive material, a magnetic material, an insulative material, a metal, a dielectric material and combinations comprising at least one of the foregoing materials.

27. The method of claim 21, wherein the material layer comprises at least one of an oxide, a nitride, a poly silicon and a chrome.

28. The method of claim 21, wherein the antireflective hardmask layer has a thickness of from about 0.03 micrometers to about five micrometers.

29. The method of claim 21, wherein the forming step comprises the step of baking the antireflective hardmask layer.

30. A patterned lithographic structure, comprising:

a substrate;

a material layer over the substrate;

a patterned antireflective hardmask layer over the material layer, the pattdmed antireflective hardmask layer comprising:

a fully condensed polyhedral oligosilsesquioxane, $\{RSiO_{1.5}\}_n$, wherein n equals 8;

at least one chromophore moiety and transparent moiety; and

a patterned radiation-sensitive imaging layer over the antireflective hardmask layer.

* * * * *

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(12) United States Patent

Angelopoulos et al.

(10) Patent No.: US 6,420,088 B1

(45) Date of Patent: Jul. 16, 2002

(54) ANTIREFLECTIVE SILICON-CONTAINING COMPOSITIONS AS HARDMASK LAYER

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 35 days.

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(52) **U.S. Cl.** **430/272.1**; 430/270.1; 430/950; 528/12; 528/13; 528/14; 528/15; 528/16; 528/17; 528/18; 528/21; 528/23; 528/25; 528/27; 528/28

(58) **Field of Search** 430/270.1, 272.1, 430/950; 528/12–18, 21, 23, 25, 27, 28

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(57) **ABSTRACT**

Antireflective compositions characterized by the presence of an SiO-containing polymer having pendant chromophore moieties are useful antireflective coating/hardmask compositions in lithographic processes. These compositions provide outstanding optical, mechanical and etch selectivity properties while being applicable using spin-on application techniques. The compositions are especially useful in lithographic processes used to configure underlying material layers on a substrate, especially metal or semiconductor layers.

8 Claims, No Drawings

ANTIREFLECTIVE SILICON-CONTAINING COMPOSITIONS AS HARDMASK LAYER

BACKGROUND OF THE INVENTION

In the microelectronics industry as well as in other industries involving construction of microscopic structures (e.g. micromachines, magnetoresistive heads, etc.), there is a continued desire to reduce the size of structural features. In the microelectronics industry, the desire is to reduce the size of microelectronic devices and/or to provide greater amount of circuitry for a given chip size.

Effective lithographic techniques are essential to achieving reduction of feature sizes. Lithography impacts the manufacture of microscopic structures not only in terms of directly imaging patterns on the desired substrate, but also in terms of making masks typically used in such imaging. Typical lithographic processes involve formation of a patterned resist layer by patternwise exposing the radiation-sensitive resist to an imaging radiation. The image is subsequently developed by contacting the exposed resist layer with a material (typically an aqueous alkaline developer) to selectively remove portions of the resist layer to reveal the desired pattern. The pattern is subsequently transferred to an underlying material by etching the material in openings of the patterned resist layer. After the transfer is complete, the remaining resist layer is then removed.

For some lithographic imaging processes, the resist used does not provide sufficient resistance to subsequent etching steps to enable effective transfer of the desired pattern to a layer underlying the resist. In many instances (e.g., where an ultrathin resist layer is desired, where the underlying material to be etched is thick, where a substantial etching depth is required, and/or where it is desired to use certain etchants for a given underlying material), a so-called hardmask layer is used intermediate between the resist layer and the underlying material to be patterned by transfer from the patterned resist. The hardmask layer receives the pattern from the patterned resist layer and should be able withstand the etching processes needed to transfer the pattern to the underlying material.

Also, where the underlying material layer is excessively reflective of the imaging radiation used to pattern the resist layer, typically a thin antireflective coating may be applied between the underlying layer and the resist layer. In some instances, the antireflection and hardmask functions may be served by the same material.

While many hardmask and antireflective coating materials exist in the prior art, there is a continued desire for improved compositions. Many of the prior art materials are difficult to apply to the substrate, e.g., they may require use of chemical or physical vapor deposition, and/or high temperature baking. It would be desirable to have antireflective coating/hardmask compositions which could be applied by spin-coating techniques without need for a high temperature bake. Additionally, it is desirable to have hardmask compositions which can be easily etched selective to the overlying photoresist while being resistant to the etch process needed to pattern the underlying layer, especially where the underlying layer is a metal layer.

SUMMARY OF THE INVENTION

The invention encompasses novel antireflective coating/hardmask compositions which are useful in lithographic processes. These compositions provide outstanding optical, mechanical and etch selectivity properties while being applicable using spin-on application techniques. The antireflective compositions are characterized by the presence of an SiO containing polymer having pendant chromophore moieties. The invention also encompasses lithographic structures containing the antireflective coating/hardmask composition of the invention, methods of making such lithographic structures and methods of using such lithographic structures to pattern underlying material layers on a substrate.

In one aspect, the invention encompasses a composition suitable for formation of a spin-on antireflective layer, the composition comprising:

(a) a polymer containing SiO moieties and chromophore moieties,

(b) a crosslinking component, and

(c) an acid generator.

The SiO moieties are preferably selected from the group consisting of siloxane moieties and silsesquioxane moieties. The SiO moieties are preferably in a backbone portion of the polymer. The SiO-containing polymer also preferably contains a plurality of reactive sites distributed along the polymer for reaction with the crosslinking component. The acid generator is preferably a thermally activated acid generator.

In another aspect, the invention encompasses a lithographic structure on a substrate, the structure comprising:

(a) an antireflective layer comprising a crosslinked polymer containing SiO moieties and chromophore moieties, and

(b) a radiation-sensitive imaging layer over the antireflective layer.

In another aspect, the invention encompasses method of forming a patterned material feature on a substrate, the method comprising:

(a) providing a material layer on a substrate,

(b) forming an antireflective layer over the material layer, the antireflective layer comprising a crosslinked polymer containing SiO moieties and chromophore moieties,

(c) forming a radiation-sensitive imaging layer over the antireflective layer,

(d) patternwise exposing the imaging layer to radiation thereby creating a pattern of radiation-exposed regions in the imaging layer,

(e) selectively removing portions of the imaging layer and the antireflective layer to expose portions of the material layer, and

(f) etching the exposed portions of the material layer, thereby forming the patterned material feature.

The material to be patterned is preferably a conductive, semiconductive, magnetic or insulative material, more preferably a metal. The SiO moieties are preferably in a backbone portion of the polymer. The SiO-containing polymer also preferably contains a plurality of reactive sites distributed along the polymer for reaction with the crosslinking component.

The invention also encompasses methods of making lithographic structures. These and other aspects of the invention are discussed in further detail below.

DETAILED DESCRIPTION OF THE INVENTION

The invention encompasses novel antireflective coating/hardmask compositions which are useful in lithographic processes. These antireflective compositions are characterized by the presence of an SiO-containing polymer having pendant chromophore moieties. The invention also encom-

passes lithographic structures containing the antireflective coating/hardmask composition of the invention, methods of making such lithographic structures and methods of using such lithographic structures to pattern underlying material layers on a substrate.

The antireflective compositions of the invention generally comprise:

(a) a polymer containing SiO moieties and chromophore moieties,

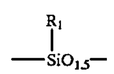
(b) a crosslinking component, and

(c) an acid generator.

The polymer containing SiO moieties may be a polymer containing SiO moieties in the polymer backbone and/or in pendant groups. Preferably, the polymer contains SiO moieties in its backbone. The polymer is preferably an organosiloxane, more preferably organosilsesquioxane. The polymer should have solution and film-forming characteristics conducive to forming a layer by conventional spin-coating. In addition to the chromophore moieties discussed below, the SiO-containing polymer also preferably contains a plurality of reactive sites distributed along the polymer for reaction with the crosslinking component.

Examples of suitable polymers include polymers having the silsesquioxane (ladder or network) structure. Such polymers preferably contain monomers having structures (I) and (II) below:

(I)



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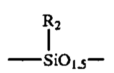
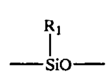


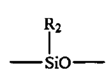
where R_1 comprises a chromophore and R_2 comprises a reactive site for reaction with the crosslinking component.

Alternatively, general linear organosiloxane polymers containing monomers (III) and (IV) can be used:

(III)

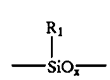


(IV)

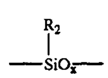


where R_1 and R_2 are as described above. In some cases, the polymer contain various combinations of monomers (I)–(IV) such that the average structure for R_1-containing monomers may be represented as structure (V) below and the average structure for R_2-containing monomers may be represented by structure (VI) below:

(V)



(VI)



where x is from about 1 to about 1.5. In theory, x may be greater than 1.5, however, such composition generally do not possess characteristics suitable for spin-coating processes (e.g., they form undesirable gel or precipitate phases).

Generally, silsesquioxane polymers are preferred on the basis of superior etch resistance. If the ordinary organosiloxane polymers are used (e.g., monomers of structures (III) and (IV)), then preferably, the degree of crosslinking is increased compared to formulations based on silsesquioxanes.

The chromophore-containing groups R_1 may contain any suitable chromophore which (i) can be grafted onto the SiO-containing polymer (ii) has suitable radiation absorption characteristics, and (iii) does not adversely affect the performance of the layer or any overlying photoresist layers. Preferred chromophore moieties include chrysenes, pyrenes, fluoranthrenes, anthrones, benzophenones, thioxanthones, and anthracenes. Anthracene derivatives, such as those described in U.S. Pat. No. 4,371,605 may also be used; the disclosure of this patent is incorporated herein by reference. 9-anthracene methanol is a preferred chromophore. The chromophore moiety preferably does not contain nitrogen, except for possibly deactivated amino nitrogen such as in phenol thiazine.

The chromophore moieties may be chemically attached to the SiO containing polymer by acid-catalyzed O-alkylation or C-alkylation such as by Friedel-Crafts alkylation. Alternatively, the chromophore moiety may be attached by an esterification mechanism. A preferred acid for Friedel-Crafts catalysis is HCl. Preferably, about 15 to 40% of the functional groups (R_1) contain chromophore moieties. In some instances, it may be possible to bond the chromophore to the monomer before formation of the SiO-containing polymer, however this is generally not preferred. The site for attachment of the chromophore is preferably an aromatic group such as a hydroxybenzyl or hydroxymethylbenzyl group. Alternatively, the chromophore may be attached by reaction with other moieties such as cyclohexanol or other alcohols. The reaction to attach the chromophore is preferably an esterification of the alcoholic OH group.

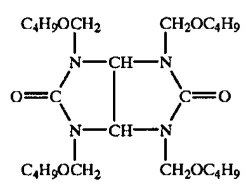
R_2 comprises a reactive site for reaction with the crosslinking component. Preferred reactive moieties contained in R_2 are alcohols, more preferably aromatic alcohols (e.g., hydroxybenzyl, phenol, hydroxymethylbenzyl, etc.) or cycloaliphatic alcohols (e.g., cyclohexanoyl). Alternatively, non-cyclic alcohols such as fluorocarbon alcohols, aliphatic alcohols, amino groups, vinyl ethers, and epoxides may be used.

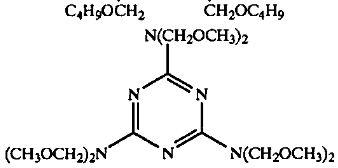
Preferably, the SiO-containing polymer (before attachment of the chromophore) is poly(4-hydroxybenzylsilsesquioxane). Examples of other silsesquioxane polymers of the invention include: poly(p-hydroxyphenylethylsilsesquioxane), poly(p-hydroxyphenylethylsilsesquioxane-co-p-hydroxy-α-methylbenzylsilsesquioxane), poly(p-hydroxyphenylethylsilsesquioxane-co-methoxybenzylsilsesquioxane), poly(p-hydroxyphenylethylsilsesquioxane-co-t-butylsilsesquioxane), poly(p-hydroxyphenylethylsilsesquioxane-co-cyclohexylsilsesquioxane), poly(p-hydroxyphenylethylsilsesquioxane-co-phenylsilsesquioxane), poly(p-hydroxyphenylethylsilsesquioxane-co-bicycloheptylsilsesquioxane), poly(p-hydroxy-α-methylbenzylsilsesquioxane), poly(p-hydroxy-α-methylbenzylsilsesquioxane-co-p-hydroxybenzylsilsesquioxane), poly(p-hydroxy-α-methylbenzylsilsesquioxane-co-methoxybenzylsilsesquioxane), poly(p-hydroxy-α-methylbenzylsilsesquioxane-co-t-butylsilsesquioxane), poly

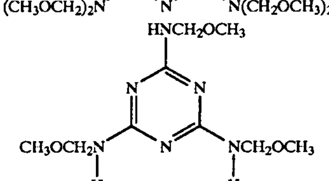
(p-hydroxy-α-methylbenzylsilsesquioxane-co-cyclohexylsilsesquioxane), poly(p-hydroxy-α-methylbenzylsilsesquioxane-co-phenylsilsesquioxane), poly(p-hydroxy-α-methylbenzylsilsesquioxane-co-bicycloheptylsilsesquioxane), and poly(p-hydroxybenzylsilsesquioxane-co-p-hydroxyphenylethylsilsesquioxane). The polyorganosiloxane polymers described in US Pat. No. 5,100,503 are generally not useful for creating low temperature bake compositions due to their very low reactivity with crosslinking components; the disclosure of this patent is incorporated herein by reference.

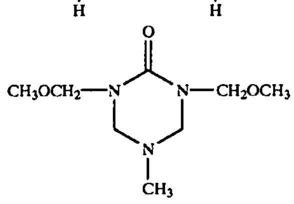
The SiO-containing polymers of the invention preferably have a weight average molecular weight, before reaction with the crosslinking component, of at least about 1000, more preferably a weight average molecular weight of about 1000–10000.

The crosslinking component is preferably a crosslinker that can be reacted with the SiO containing polymer in a manner which is catalyzed by generated acid and/or by heating. Generally, the crosslinking component used in the antireflective compositions of the invention may be any suitable crosslinking agent known in the negative photoresist art which is otherwise compatible with the other selected components of the composition. The crosslinking agents preferably act to crosslink the polymer component in the presence of a generated acid. Preferred crosslinking agents are glycoluril compounds such as tetramethoxymethyl glycoluril, methylpropyltetramethoxymethyl glycoluril, and methylphenyltetramethoxymethyl glycoluril, available under the POWDERLINK trademark from American Cyanamid Company. Other possible crosslinking agents include: 2,6-bis(hydroxymethyl)-p-cresol, compounds having the following structures:









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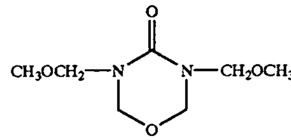

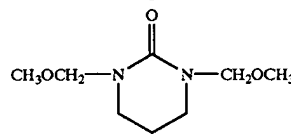

including their analogs and derivatives, such as those found in Japanese Laid-Open Patent Application (Kokai) No. 1-293339, as well as etherified amino resins, for example methylated or butylated melamine resins (N-methoxymethyl- or N-butoxymethyl-melamine respectively) or methylated/butylated glycolurils, for example as can be found in Canadian Patent No. 1 204 547. Other crosslinking agents such as bis-epoxies or bis-phenols (e.g., bisphenol-A) may also be used. Combinations of crosslinking agents may be used.

The acid generator is preferably an acid generator compound is employed that liberates acid upon thermal treatment. A variety of known thermal acid generators are suitably employed such as e.g. 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate and other alkyl esters of organic sulfonic acids. Compounds that generate a sulfonic acid upon activation are generally suitable. Other suitable thermally activated acid generators are described in U.S. Pat. Nos. 5,886,102 and 5,939,236; the disclosures of these two patents are incorporated herein by reference. If desired, a radiation-sensitive acid generator may be employed as an alternative to a thermally activated acid generator or in combination with a thermally activated acid generator. Examples of suitable radiation-sensitive acid generators are described in U.S. Pat. Nos. 5,886,102 and 5,939,236. Other radiation-sensitive acid generators known in the resist art may also be used as long as they are compatible with the other components of the antireflective composition. Where a radiation-sensitive acid generator is used, the cure (crosslinking) temperature of the composition may be reduced by application of appropriate radiation to induce acid generation which in turn catalyzes the crosslinking reaction. Even if a radiation-sensitive acid generator is used, it is preferred to thermally treat the composition to accelerate the crosslinking process (e.g., for wafers in a production line).

The antireflective compositions of the invention preferably contain (on a solids basis) (i) about 50–98 wt. % of the SiO-containing polymer, more preferably about 70–80 wt. %, (ii) about 1–50 wt. % of crosslinking component, more preferably about 3–25%, most preferably about 5–25 wt. %, and (iii) about 1–20 wt. % acid generator, more preferably about 1–15 wt. %.

The antireflective coating/hardmask compositions of the invention may be used in combination with any desired resist material in the forming of a lithographic structure. Preferably, the resist is imageable with ultraviolet radiation (e.g.<400 nm wavelength) or with electron beam radiation. Examples of suitable resist materials are described in U.S. Pat. Nos. 5,861,231; 5,962,184; and 6,037,097, the disclosures of which are incorporated herein by reference.

The antireflective compositions of the invention will typically contain a solvent prior to their application to the

desired substrate. The solvent may be any solvent conventionally used with resists which otherwise does not have any excessively adverse impact on the performance of the antireflective composition. Preferred solvents are propylene glycol monomethyl ether acetate, cyclohexanone, and ethyl cellosolve acetate. The amount of solvent in the composition for application to a substrate is preferably sufficient to achieve a solids content of about 8–20 wt. %. Higher solids content formulations will generally yield thicker coating layers. The compositions of the invention may further contain minor amounts of auxiliary components (e.g., base additives, etc.) as may be known in the art.

The antireflective compositions of the invention can be prepared by combining the polymer, crosslinking component and acid generator, and any other desired ingredients using conventional methods. The compositions of the invention advantageously may be formed into antireflective layers on a substrate by spin-coating followed by baking to achieve crosslinking and solvent removal. The baking is preferably conducted at about 250° C. or less, more preferably about 150°–200° C., most preferably about 170°–180° C. The baking time may be varied depending on the layer thickness and bake temperature. A typical time at 170° would be about two minutes. The thickness of the antireflective composition of the invention may be varied depending on the desired function. For example, where the composition is used as a non-planarizing antireflective coating, the thickness may be about 50–500 nm. Where the composition is used as a planarizing hardmask, the thickness is preferably about 0.5–5.0 μm. If desired, the compositions of the invention may also be used as dielectric materials in a similar manner to conventional spin-on glass materials.

The compositions of the invention are especially useful for lithographic processes used in the manufacture of integrated circuits on semiconductor substrates. The compositions are especially useful for lithographic processes using mid-UV, 248 nm deep UV, x-ray, or e-beam or other imaging radiation.

Semiconductor lithographic applications generally involve transfer of a pattern to a layer of material on the semiconductor substrate. The material layer of the semiconductor substrate may be a metal conductor layer, a ceramic insulator layer, a semiconductor layer or other material depending on the stage of the manufacture process and the desired material set for the end product. The composition of the invention is preferably applied directly over the material layer to be patterned, preferably by spin-coating. The composition is then baked to remove solvent and cure (crosslink) the composition. A radiation-sensitive resist layer can then be applied (directly or indirectly) over the cured antireflective composition of the invention.

Typically, the solvent-containing resist composition is applied using spin coating or other technique. The substrate with the resist coating is then preferably heated (pre-exposure baked) to remove the solvent and improve the coherence of the resist layer. The thickness of the applied layer is preferably as thin as possible with the provisos that the thickness is preferably substantially uniform and that the resist layer be sufficient to withstand subsequent processing (typically reactive ion etching) to transfer the lithographic pattern to the underlying substrate material layer. The pre-exposure bake step is preferably conducted for about 10 seconds to 15 minutes, more preferably about 15 seconds to one minute. The pre-exposure bake temperature may vary depending on the glass transition temperature of the photoresist.

After solvent removal, the resist layer is then patternwise-exposed to the desired radiation (e.g. 248 nm ultraviolet radiation). Where scanning particle beams such as electron beam are used, patternwise exposure may be achieved by scanning the beam across the substrate and selectively applying the beam in the desired pattern. More typically, where wavelike radiation forms such as 248 nm ultraviolet radiation, the patternwise exposure is conducted through a mask which is placed over the resist layer. For 248 nm UV radiation, the total exposure energy is preferably about 100 millijoules/cm^2 or less, more preferably about 50 millijoules/cm^2 or less (e.g. 15–30 millijoules/cm^2).

After the desired patternwise exposure, the resist layer is typically baked to further complete the acid-catalyzed reaction and to enhance the contrast of the exposed pattern. The post-exposure bake is preferably conducted at about 60–175° C., more preferably about 90–160° C. The post-exposure bake is preferably conducted for about 30 seconds to 5 minutes.

After post-exposure bake, the resist structure with the desired pattern is obtained (developed) by contacting the resist layer with an alkaline solution which selectively dissolves the areas of the resist which were exposed to radiation. Preferred alkaline solutions (developers) are aqueous solutions of tetramethyl ammonium hydroxide. The resulting lithographic structure on the substrate is then typically dried to remove any remaining developer solvent.

The pattern from the resist structure may then be transferred to the exposed portions of the layer of antireflective material of the invention by etching with CF_4 or other suitable etchant using techniques known in the art.

After the opening of the layer of antireflective material of the invention and any underlying antireflective coating, the underlying material layer to be patterned may then be etched using an etchant appropriate to the material layer composition. Where the material layer is a metal (e.g., Cr) a combination of Cl_2/O_2 may be used as a dry etchant. Once the desired pattern transfer has taken place, any remaining resist may be removed using conventional stripping techniques. If the composition of the invention is being used strictly as a hardmask or non-planarizing antireflective coating, the composition of the invention may be removed by contacting with a CF_4/O_2 plasma.

Thus, the compositions of the invention and resulting lithographic structures can be used to create patterned material layer structures such as metal wiring lines, holes for contacts or vias, insulation sections (e.g., damascene trenches or shallow trench isolation), trenches for capacitor structures, etc. as might be used in the design of integrated circuit devices. The compositions are especially useful in the context of creating patterned metal structures, especially Cr-based structures useful as masks.

Examples of general lithographic processes where the composition of the invention may be useful are disclosed in U.S. Pat. Nos. 4,855,017; 5,362,663; 5,429,710; 5,562,801; 5,618,751; 5,744,376; 5,801,094; 5,821,469 and 5,948,570, the disclosures of which patents are incorporated herein by reference. Other examples of pattern transfer processes are described in Chapters 12 and 13 of "Semiconductor Lithography, Principles, Practices, and Materials" by Wayne Moreau, Plenum Press, (1988), the disclosure of which is incorporated herein by reference. It should be understood that the invention is not limited to any specific lithography technique or device structure.

EXAMPLE 1

Ortho Grafting of 9-anthracenemethyl Group to Poly(4-hydroxybenzylsilsesquioxane) and the Formulation of Hardmask/antireflective Layer.

9-anthracene methanol 6.7 g was reacted with 16 g of poly(4-hydroxybenzylsilsesquioxane) in 150 g of acetoni-

trile containing 0.4 g of HCl. The solution was heated to reflux for several hours, and then water was added to precipitate the grafted polymer. The dried polymer was dissolved as a 14 wt. % solution in propylene glycol monomethyl ether acetate (PGMEA). Glycoluril resin (POWDERLINK crosslinking agent) and nitrobenzyl tosylate (acid generator) were added to the solution in amounts to achieve 10 wt. % of total solids and 5 wt. % of solids respectively. 200 ppm of FC430 surfactant (sold by 3M Corporation) was also added to the solution.

EXAMPLE 2

Etching the Hardmask/antireflective Layer vs. UV-80 with CF_4/O_2 Gas

The hardmask/antireflective layer (HM/ARC), formulated as described in Example 1, was spin-coated on hexamethyldisilazane(HMDS)-primed wafer at 3000 rpm. The spun film was cured at 175° C. for 3 minutes. A layer of UV-80 photoresist (sold by Shipley Company) was spin-coated over the cured layer at 3000 rpm. The photoresist layer was soft baked at 130° C. for 60 seconds.

Thickness measurements were made with a profilometer. To make the thickness measurements, a 13.0 nm Al strip was used as a mask; this Al is not etched in the Cl_2/O_2 or in the CF_4/O_2 plasmas.

A generic oxide etch process was used in the CF_4/O_2 etch with the conditions of Table I. A low pressure, high density plasma process using an inductively coupled plasma (ICP) was used. Flow rate, pressure, power and Ar dilution were selected to give a relatively stable process without the oscillations frequently encountered with these electronegative discharges. The DC self bias voltage was kept to 150 volts.

TABLE I

Etch condition for CF_4/O_2	
CF_4 flow	40 sccm
O_2 flow	6 sccm
Ar flow	25 sccm
etch pressure	6.1 mT
ICP power	400 W
rf substrate power	30 W
dc bias voltage	-150 V

TABLE II

Etch thickness and etch rate			
Etch time	45s	50s	90s
UV80	179 nm (4.0 nm/s)	227 nm (4.5 nm/s)	402 nm (4.5 nm/s)
HM/ARC	157 nm (3.5 nm/s)	205 nm (4.1 nm/s)	>374 nm (>4.2 nm/s)

EXAMPLE 3

Etching the Hardmask/antireflective Layer vs. UV80 with Cl_2/O_2 Gas

Both HM/ARC and UV80 were processed as Example 2 except the etching process which is described in Table III.

TABLE III

Etch condition for Cl_2/O_2	
Cl_2 flow	24 sccm
O_2 flow	6 sccm
Ar flow	25 sccm
etch pressure	12 mT
ICP power	500 W
rf substrate power	12 W
dc bias voltage	-114 V

The etch rate of HM/ARC is significantly lower than UV-80.

TABLE IV

Etch thickness and etch rate		
Etch time	50s	150s
UV80	61 nm (1.2 nm/s)	237 nm (1.5 nm/s)
HM/ARC	20 nm (0.4 nm/s)	46 nm (0.3 nm/s)

What is claimed is:

1. A composition suitable for formation of a spin-on antireflective layer, said composition comprising:

(a) a polymer containing SiO moieties, a plurality of reactive sites distributed along the polymer for reaction with a crosslinking component, and chromophore moieties,

(b) a crosslinking component, and

(c) an acid generator.

2. The composition of claim 1 wherein said SiO moieties are selected from the group consisting of siloxane moieties and silsesquioxane moieties.

3. The composition of claim 1 wherein said acid generator is a thermally activated acid generator.

4. The composition of claim 1 wherein said chromophore moieties are selected from the group consisting of chrysenes, pyrenes, fluoranthrenes, anthrones, benzophenones, thioxanthones, and anthracenes.

5. The composition of claim 1 wherein said crosslinking component comprises a glycoluril compound.

6. The composition of claim 1 wherein said composition consists essentially of components (a), (b), and (c).

7. The composition of claim 1 wherein said SiO moieties are in a backbone portion of said polymer.

8. The composition of claim 1 wherein said composition contains about 50–98 wt. % of (a), about 1–50 wt. % of (b), and about 1–20 wt. % of (c).

* * * * *

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(12) **United States Patent**
Pfeiffer et al.

(10) **Patent No.: US 6,730,454 B2**
(45) **Date of Patent: May 4, 2004**

(54) **ANTIREFLECTIVE SIO-CONTAINING COMPOSITIONS FOR HARDMASK LAYER**

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(52) **U.S. Cl.** **430/270.1**; 430/271.1; 430/272.2; 430/311; 430/313; 430/510; 430/512; 430/950

(58) **Field of Search** 430/311, 313, 430/322, 270.1, 271.1, 272.2, 510, 512, 950

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(57) **ABSTRACT**

Antireflective compositions characterized by the presence of an SiO-containing polymer having chromophore moieties and transparent moieties are useful antireflective hardmask compositions in lithographic processes. These compositions provide outstanding optical, mechanical and etch selectivity properties while being applicable using spin-on application techniques. The compositions of the invention are advantageously useful with shorter wavelength lithographic processes and/or have minimal residual acid content.

11 Claims, No Drawings

ANTIREFLECTIVE SIO-CONTAINING COMPOSITIONS FOR HARDMASK LAYER

BACKGROUND OF THE INVENTION

In the microelectronics industry as well as in other industries involving construction of microscopic structures (e.g. micromachines, magnetoresistive heads, etc.), there is a continued desire to reduce the size of structural features. In the microelectronics industry, the desire is to reduce the size of microelectronic devices and/or to provide greater amount of circuitry for a given chip size.

Effective lithographic techniques are essential to achieving reduction of feature sizes. Lithography impacts the manufacture of microscopic structures not only in terms of directly imaging patterns on the desired substrate, but also in terms of making masks typically used in such imaging. Typical lithographic processes involve formation of a patterned resist layer by patternwise exposing the radiation-sensitive resist to an imaging radiation. The image is subsequently developed by contacting the exposed resist layer with a material (typically an aqueous alkaline developer) to selectively remove portions of the resist layer to reveal the desired pattern. The pattern is subsequently transferred to an underlying material by etching the material in openings of the patterned resist layer. After the transfer is complete, the remaining resist layer is then removed.

For some lithographic imaging processes, the resist used does not provide sufficient resistance to subsequent etching steps to enable effective transfer of the desired pattern to a layer underlying the resist. In many instances (e.g., where an ultrathin resist layer is desired, where the underlying material to be etched is thick, where a substantial etching depth is required, and/or where it is desired to use certain etchants for a given underlying material), a so-called hardmask layer is used intermediate between the resist layer and the underlying material to be patterned by transfer from the patterned resist. The hardmask layer receives the pattern from the patterned resist layer and should be able withstand the etching processes needed to transfer the pattern to the underlying material.

While many hardmask materials exist in the prior art, there is a continued desire for improved hardmask compositions. Many of the prior art materials are difficult to apply to the substrate, e.g., they may require use of chemical or physical vapor deposition, special solvents, and/or high temperature baking. It would be desirable to have hardmask compositions which could be applied by spin-coating techniques without need for a high temperature bake. Additionally, it is desirable to have hardmask compositions which can be easily etched selective to the overlying photoresist while being resistant to the etch process needed to pattern the underlying layer, especially where the underlying layer is a metal layer. It is also desired to provide adequate shelf-life and to avoid adverse interaction with the imaging resist layer (e.g., by acid contamination from the hardmask). Additionally, it is desired to have hardmask compositions which possess the desired optical characteristics relative to shorter wavelength (e.g., <200 nm) imaging radiation.

SUMMARY OF THE INVENTION

The invention encompasses novel antireflective hardmask compositions which are useful in lithographic processes. These compositions provide outstanding optical, mechanical and etch selectivity properties while being applicable using spin-on application techniques. The compositions also have

good shelf-life and minimal or no acid contaminant content. The antireflective hardmask compositions are characterized by the presence of an SiO-containing polymer having chromophore moieties and transparent moieties. The invention also encompasses methods of using the hardmask compositions of the invention to pattern underlying material layers on a substrate. The invention also encompasses lithographic structures such as a patterned combination of resist layer and hardmask layer.

In one aspect, the invention encompasses a composition suitable for formation of a spin-on antireflective hardmask layer, the composition comprising:

(a) an SiO-containing polymer having chromophore moieties and transparent moieties,

(b) a crosslinking component, and

(c) an acid generator.

The SiO moieties are preferably selected from the group consisting of siloxane moieties and silsesquioxane moieties. The SiO moieties are preferably in a backbone portion of the polymer. The SiO-containing polymer also preferably contains a plurality of reactive sites distributed along the polymer for reaction with the crosslinking component. The acid generator is preferably a thermally activated acid generator. The transparent moieties are preferably bulky (C_2 or higher) or fluorine-containing moieties which are substantially transparent to the desired imaging radiation.

In another aspect, the invention encompasses method of forming a patterned material feature on a substrate, the method comprising:

(a) providing a material layer on a substrate,

(b) forming an antireflective hardmask layer of the invention over the material layer,

(c) forming a radiation-sensitive imaging layer over the antireflective layer,

(d) patternwise exposing the imaging layer to radiation thereby creating a pattern of radiation-exposed regions in the imaging layer,

(e) selectively removing portions of the imaging layer and the antireflective layer to expose portions of the material layer, and

(f) etching the exposed portions of the material layer, thereby forming the patterned material feature.

The material to be patterned is preferably a conductive, semiconductive, magnetic or insulative material, more preferably a metal. The SiO moieties are preferably in a backbone portion of the polymer. The SiO-containing polymer also preferably contains a plurality of reactive sites distributed along the polymer for reaction with the crosslinking component.

These and other aspects of the invention are discussed in further detail below.

DETAILED DESCRIPTION OF THE INVENTION

The invention encompasses novel antireflective hardmask compositions which are useful in lithographic processes. These antireflective hardmask compositions are characterized by the presence of an SiO-containing polymer having chromophore moieties and transparent moieties. The invention also encompasses methods of using the antireflective hardmask compositions of the invention to pattern underlying material layers on a substrate. The invention also encompasses lithographic structures such as a patterned combination of resist layer and hardmask layer.

The antireflective hardmask compositions of the invention generally comprise:

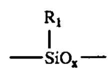
(a) an SiO-containing polymer having chromophore moieties and transparent moieties,

(b) a crosslinking component, and

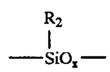
(c) an acid generator.

The SiO-containing polymer preferably contains SiO moieties in its backbone. The polymer is preferably an organosiloxane, more preferably organosilsesquioxane. The polymer should have solution and film-forming characteristics conducive to forming a layer by conventional spin-coating.

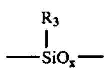
In general, the polymer preferably contains one or more monomers having structures selected from (I)–(III) below:



(I)



(II)



(III)

where x is from about 1 to about 1.5. R_1 comprises a chromophore moiety; R_2 comprises a transparent moiety; R_3 comprises a reactive site for reaction with the crosslinking component. For linear organosiloxane polymers, x would equal about 1. For silsesquioxane polymers, x would equal about 1.5. In some instances, multiple functional moieties may be present on the same monomer (e.g., a reactive group and a chromophore). Generally, silsesquioxane polymers are preferred on the basis of superior etch resistance. If the ordinary organosiloxane polymers are used, then preferably, the degree of crosslinking is increased compared to formulations based on silsesquioxanes.

The chromophore-containing groups R_1 may contain any suitable chromophore which (i) can be grafted onto the SiO-containing polymer (ii) has suitable radiation absorption characteristics, and (iii) does not adversely affect the performance of the layer or any overlying photoresist layers. Preferred chromophore moieties include phenyl, chrysenes, pyrenes, fluoranthrenes, anthrones, benzophenones, thioxanthones, and anthracenes. Anthracene derivatives, such as those described in U.S. Pat. No. 4,371,605 may also be used; the disclosure of this patent is incorporated herein by reference. 9-anthracene methanol is a preferred chromophore. The chromophore moiety preferably does not contain nitrogen, except for possibly deactivated amino nitrogen such as in phenol thiazine. For 193 nm radiation, non-aromatic compounds containing unsaturated carbon bonds (e.g., carbon—carbon double bonds) are also suitable chromophores. For 157 nm radiation, compounds containing saturated carbon—carbon bonds can act as chromophores.

The chromophore moieties may be chemically attached to the SiO containing polymer by acid-catalyzed O-alkylation or C-alkylation such as by Friedel-Crafts alkylation. Alternatively, the chromophore moiety may be attached by an esterification mechanism. A preferred acid for Friedel-Crafts catalysis is HCl. Preferably, about 15 to 40% of the monomers contain chromophore moieties. In some instances, it may be possible to bond the chromophore to the monomer before formation of the SiO-containing polymer, however this is generally not preferred. The site for attachment of the chromophore is preferably an aromatic group such as a hydroxybenzyl or hydroxymethylbenzyl group. Alternatively, the chromophore may be attached by reaction with other moieties such as cyclohexanol or other alcohols. The reaction to attach the chromophore is preferably an esterification of the alcoholic OH group.

R_2 transparent moieties may vary depending on the wavelength or character of the imaging radiation. In the case of 193 nm imaging radiation, the transparent moieties are preferably a bulky (C_2 or higher) organic moieties substantially free of unsaturated carbon—carbon bonds. A preferred transparent moiety for 193 nm applications in an alcohol derived from an epoxy-functionalized silsesquioxane monomer. In the case of 157 nm imaging radiation, the transparent moieties are preferably fluorine-containing moieties such as a trifluoromethyl group or perfluoroalkyl. The amount of transparent moieties is preferably balanced with the amount of chromophore to provide a desired combination of energy absorption and antireflection.

R_3 comprises a reactive site for reaction with the crosslinking component. Preferred reactive moieties contained in R_2 are alcohols, more preferably aromatic alcohols (e.g., hydroxybenzyl, phenol, hydroxymethylbenzyl, etc.) or cycloaliphatic alcohols (e.g., cyclohexanoyl). Alternatively, non-cyclic alcohols such as fluorocarbon alcohols, aliphatic alcohols, amino groups, vinyl ethers, and epoxides may be used.

Examples of SiO containing polymers include:

poly(3-propanoloxypropyl)silsesquioxane, copolymer of 3-propanoloxypropylsilsesquioxane and phenylsilsesquioxane, blend of poly(hydroxybenzyl) silsesquioxane and poly(1-hydroxy-1-trifluoromethylethyl) silsesquioxane, copolymer of 1-hydroxy-1-trifluoromethylethylsilsesquioxane and p-Hydroxymethylbenzylsilsesquioxane.

The SiO-containing polymers of the invention preferably have a weight average molecular weight, before reaction with the crosslinking component, of at least about 1000, more preferably a weight average molecular weight of about 1000–10000.

The crosslinking component is preferably a crosslinker that can be reacted with the SiO-containing polymer in a manner which is catalyzed by generated acid and/or by heating. Generally, the crosslinking component used in the antireflective hardmask compositions of the invention may be any suitable crosslinking agent known in the negative photoresist art which is otherwise compatible with the other selected components of the composition. The crosslinking agents preferably act to crosslink the polymer component in the presence of a generated acid. Preferred crosslinking agents are glycoluril compounds such as tetramethoxymethyl glycoluril, methylpropyltetramethoxymethyl glycoluril, and methylphenyltetramethoxymethyl glycoluril, available under the POWDERLINK trademark from Cytec Industries. Other possible crosslinking agents include: 2,6-bis(hydroxymethyl)-p-cresol compounds such as those found in Japanese Laid-Open Patent Application (Kokai) No. 1-293339, etherified amino resins, for example methylated or butylated melamine resins (N-methoxymethyl- or N-butoxymethyl-melamine respectively), and methylated/butylated glycolurils, for example as can be found in Canadian Patent No. 1 204 547. Other crosslinking agents such as bis-epoxies or bis-phenols (e.g., bisphenol-A) may also be used. Combinations of crosslinking agents may be used.

The acid generator is preferably an acid generator compound is employed that liberates acid upon thermal treatment. A variety of known thermal acid generators are suitably employed such as e.g. 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-nitrobenzyl tosylate and other alkyl esters of organic

sulfonic acids. Compounds that generate a sulfonic acid upon activation are generally suitable. Other suitable thermally activated acid generators are described in U.S. Pat. Nos. 5,886,102 and 5,939,236; the disclosures of these two patents are incorporated herein by reference. If desired, a radiation-sensitive acid generator may be employed as an alternative to a thermally activated acid generator or in combination with a thermally activated acid generator. Examples of suitable radiation-sensitive acid generators are described in U.S. Pat. Nos. 5,886,102 and 5,939,236. Other radiation-sensitive acid generators known in the resist art may also be used as long as they are compatible with the other components of the antireflective composition. Where a radiation-sensitive acid generator is used, the cure (crosslinking) temperature of the composition may be reduced by application of appropriate radiation to induce acid generation which in turn catalyzes the crosslinking reaction. Even if a radiation-sensitive acid generator is used, it is preferred to thermally treat the composition to accelerate the crosslinking process (e.g., for wafers in a production line).

The antireflective hardmask compositions of the invention preferably contain (on a solids basis) (i) about 50–98 wt. % of the SiO-containing polymer, more preferably about 70–80 wt. %, (ii) about 1–50 wt. % of crosslinking component, more preferably about 3–25%, and (iii) about 1–20 wt. % acid generator, more preferably about 1–15 wt. %.

The antireflective hardmask compositions of the invention may be used in combination with any desired resist material in the forming of a lithographic structure. Preferably, the resist is imageable with shorter wavelength ultraviolet radiation (e.g. <200 nm wavelength) or with electron beam radiation. Examples of suitable resist materials are described in U.S. Pat. No. 6,037,097, the disclosure of which is incorporated herein by reference.

The antireflective hardmask compositions of the invention will typically contain a solvent prior to their application to the desired substrate. The solvent may be any solvent conventionally used with resists which otherwise does not have any excessively adverse impact on the performance of the antireflective composition. Preferred solvents are propylene glycol monomethyl ether acetate, cyclohexanone, and ethyl lactate. The amount of solvent in the composition for application to a substrate is preferably sufficient to achieve a solids content of about 8–20 wt. %. Higher solids content formulations will generally yield thicker coating layers. The compositions of the invention may further contain minor amounts of auxiliary components (e.g., base additives, etc.) as may be known in the art.

The antireflective hardmask compositions of the invention can be prepared by combining the polymer, crosslinking component and acid generator, and any other desired ingredients using conventional methods. The compositions of the invention advantageously may be formed into antireflective hardmask layers on a substrate by spin-coating followed by baking to achieve crosslinking and solvent removal. The baking is preferably conducted at about 250° C. or less, more preferably about 150°–220° C. The baking time may be varied depending on the layer thickness and bake temperature.

The thickness of the antireflective hardmask composition of the invention may be varied depending on the desired function. For typical applications, the thickness of the composition is preferably about 0.02–5.0 μm, more preferably about 0.1–5.0 μm. If desired, the compositions of the invention may also be used as dielectric materials in a similar manner to conventional spin-on glass materials. The compositions of the invention advantageously resist lateral etch such that they may act as hard masks even at thin film thickness traditionally associated with organic antireflective layers.

The hardmask compositions of the invention are especially useful for lithographic processes used in the manufacture of integrated circuits on semiconductor substrates. The compositions are especially useful for lithographic processes using 193 nm, 157 nm, EUV, x-ray, e-beam or other imaging radiation.

Semiconductor lithographic applications generally involve transfer of a pattern to a layer of material on the semiconductor substrate. The material layer of the semiconductor substrate may be a metal conductor layer, a ceramic insulator layer, a semiconductor layer or other material depending on the stage of the manufacture process and the desired material set for the end product. The composition of the invention is preferably applied directly over the material layer to be patterned, preferably by spin-coating. The composition is then baked to remove solvent and cure (crosslink) the composition. A radiation-sensitive resist layer can then be applied (directly or indirectly) over the cured antireflective composition of the invention.

Typically, the solvent-containing resist composition is applied using spin coating or other technique. The substrate with the resist coating is then preferably heated (pre-exposure baked) to remove the solvent and improve the coherence of the resist layer. The thickness of the applied layer is preferably as thin as possible with the provisos that the thickness is preferably substantially uniform and that the resist layer be sufficient to withstand subsequent processing (typically reactive ion etching) to transfer the lithographic pattern to the underlying substrate material layer. The pre-exposure bake step is preferably conducted for about 10 seconds to 15 minutes, more preferably about 15 seconds to one minute. The pre-exposure bake temperature may vary depending on the glass transition temperature of the photoresist.

After solvent removal, the resist layer is then patternwise-exposed to the desired radiation (e.g. 193 nm ultraviolet radiation). Where scanning particle beams such as electron beam are used, patternwise exposure may be achieved by scanning the beam across the substrate and selectively applying the beam in the desired pattern. More typically, where wavelike radiation forms such as 193 nm ultraviolet radiation, the patternwise exposure is conducted through a mask which is placed over the resist layer. For 193 nm UV radiation, the total exposure energy is preferably about 100 millijoules/cm^2 or less, more preferably about 50 millijoules/cm^2 or less (e.g. 15–30 millijoules/cm^2).

After the desired patternwise exposure, the resist layer is typically baked to further complete the acid-catalyzed reaction and to enhance the contrast of the exposed pattern. The post-exposure bake is preferably conducted at about 60–175° C., more preferably about 90–160° C. The post-exposure bake is preferably conducted for about 30 seconds to 5 minutes.

After post-exposure bake, the resist structure with the desired pattern is obtained (developed) by contacting the resist layer with an alkaline solution which selectively dissolves the areas of the resist which were exposed to radiation. Preferred alkaline solutions (developers) are aqueous solutions of tetramethyl ammonium hydroxide. The resulting lithographic structure on the substrate is then typically dried to remove any remaining developer solvent.

The pattern from the resist structure may then be transferred to the exposed portions of the layer of antireflective

material of the invention by etching with CF_4 or other suitable etchant using techniques known in the art.

After the opening of the layer of antireflective hardmask of the invention, the underlying material layer to be patterned may then be etched using an etchant appropriate to the material layer composition. Where the material layer is a metal (e.g., Cr) a combination of Cl_2/O_2 may be used as a dry etchant.

Once the desired pattern transfer has taken place, any remaining resist may be removed using conventional stripping techniques. If the composition of the invention is being used strictly as a hardmask, the composition of the invention may be removed by contacting with a CF_4/O_2 plasma.

Thus, the compositions of the invention and resulting lithographic structures can be used to create patterned material layer structures such as metal wiring lines, holes for contacts or vias, insulation sections (e.g., damascene trenches or shallow trench isolation), trenches for capacitor structures, etc. as might be used in the design of integrated circuit devices. The compositions are especially useful in the context of creating patterned layers of oxides, nitrides or polysilicon.

Examples of general lithographic processes where the composition of the invention may be useful are disclosed in U.S. Pat. Nos. 4,855,017; 5,362,663; 5,429,710; 5,562,801; 5,618,751; 5,744,376; 5,801,094; 5,821,469 and 5,948,570, the disclosures of which patents are incorporated herein by reference. Other examples of pattern transfer processes are described in Chapters 12 and 13 of "Semiconductor Lithography, Principles, Practices, and Materials" by Wayne Moreau, Plenum Press, (1988), the disclosure of which is incorporated herein by reference. It should be understood that the invention is not limited to any specific lithographic technique or device structure.

EXAMPLE 1

(Polymer A)

The silicone precursor 3-glycidoxypropyltrimethoxysilane (47.26 g, 200 mmol) (available from Aldrich) was dissolved in 100 ml of tetrahydrofuran (THF) and then hydrolyzed by a mixture of THF and 1 N HCl at room temperature. The reaction mixture was then refluxed for 18 hours to complete the hydrolysis. After cooling down to room temperature, 150 ml of diethylether were added and the aqueous phase was separated from the organic phase and discarded. The organic phase was washed with brine (50 ml) twice and dried over magnesium sulfate, followed by removal of the solvent in vacuum, leaving the polymer as a clear viscous oil behind. The polymer was dried in vacuum and the final yield was ca. 27 g. The material was characterized by NMR and IR, showing that the epoxy functional group was converted to an alcohol functional group.

(Polymer B)

The silicone precursors phenyltrimethoxysilane (7.92 g, 40 mmol) and 3-glycidoxypropyltrimethoxysilane (37.82 g, 160 mmol) (both available from Aldrich) were reacted in the same manner described in for Polymer A to give the polymer in a final yield of ca. 25 g.

(Polymer C)

Poly(hydroxybenzyl)silsesquioxane (PHBSQ —obtained from DayChem Laboratories in Vandalia, Ohio)

(Polymer D)

Poly(1-Hydroxy-1-Trifluoromethylethyl) silsesquioxane (TFASSQ) was synthesized according to the procedure of U.S. patent application Ser. No. 09/748071 ("Substantially Transparent Aqueous Base Soluble Polymer System For Use In 157 nm Resist Applications") filed Dec. 21, 2000, published as U.S. 2002/0081520.

EXAMPLE 2

Formulation

The desired SiO-containing polymer component was dissolved in propylene glycol monomethyl ether acetate (PGMEA) in concentrations of 100 parts by weight. A crosslinking agent tetramethoxymethyl glycoluril, available from DayChem, in a concentration of 8 parts by weight and di(t-butylphenyl)iodoniumperfluorobutylsulfonate (DtBPI-PFBuS) in a concentration of 4 parts by weight were added to the solution, achieving 14 wt. % of total solids.

EXAMPLE 3

Film Formation and Optical Properties

Formulations, prepared as described in Example 2, were spin coated onto a 300 mm silicon wafer at 3000 rpm for 60 sec. The film thickness was about 2500 Å. The spin cast film was cured at 200° C. for 60 sec. The optical constants (the index of refraction n and the extinction coefficient k at 193 nm) are measured using an n&k Analyzer manufactured by n&k Technology, Inc.

The optical properties of the films for 193 nm radiation were as follows:

Film Polymer	n	K
Polymer A	1.656	0.006
Polymer B	1.726	0.390
Polymer C	1.556	0.000
Polymers C & D (1:1 wt/wt)	1.689	0.205

EXAMPLE 4

Shelf Life Study

A formulation described in Example 2 using Polymer B was divided into two batches. One batch was stored at −20° C. over period of one month and the other batch was stored at 40° C. over period of one month. The reflectance spectra of two films from each batch formed by the method described in Example 3 are identical demonstrating the formulation has not aged.

EXAMPLE 5

193 nm Lithography and Etching the Hardmask/antireflective Layer

The hardmask layer was formed as described in Example 3 using the Polymer B. A layer of PAR 715 acrylic-based photoresist (sold by Sumitomo) was spin-coated over the cured hardmask layer to a thickness of about 250 nm. The photoresist was baked at 130° C. for 60 seconds. The resist layer was then imaged using a 0.6 NA 193 nm Nikon Stepper with conventional and annular illumination using APSM reticle. After patternwise exposure, the resist was baked at 130° C. for 60 seconds. The image was then developed using commercial developer (0.26M TMAH). The resulting pattern showed 113.75 and 122.5 nm equal lines and space patterns.

The pattern was then transferred into the hard mask layer by a 20 second fluorocarbon based etch using a TEL DRM tool. The etch selectivity between the photoresist and the hardmask exceeded 10:1, demonstrating that virtually no resist is lost during the hardmask open etch.

The etch selectivity of the oxide to hardmask (Polymer B) was determined on blanket films to be 2.5:1 and 3.3:1 for the resist (PAR 715) to oxide, respectively, using a fluorocarbon based etch performed on a TEL DRM tool. The combined etch selectivities will give an overall etch selectivity of the pattern transfer from oxide to organic resist >20:1 which is superior to any known organic hardmasks.

What is claimed is:

1. A composition suitable for formation of a spin-on antireflective hardmask layer, said composition comprising:

(a) an SiO-containing polymer (i) having a backbone containing SiO moieties, (ii) having chromophore moieties, and (iii) having transparent moieties,

(b) a separate crosslinking component, and

(c) an acid generator.

2. The composition of claim 1 wherein said transparent moieties are substantially free of unsaturated carbon—carbon bonds.

3. The composition of claim 1 wherein said chromophore moieties contain unsaturated carbon—carbon bonds.

4. The composition of claim 1 wherein said composition transparent moieties are substantially transparent to 157 nm radiation.

5. The composition of claim 4 wherein said transparent moieties are selected from the group consisting of perfluoroalkyl and trifluoromethyl.

6. The composition of claim 1 wherein said acid generator is a thermally activated acid generator.

7. The composition of claim 1 wherein said SiO-containing polymer further comprises a plurality of reactive sites distributed along the polymer for reaction with the crosslinking components.

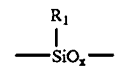
8. The composition of claim 1 wherein said chromophore moieties are selected from the group consisting of phenyl, chrysenes, pyrenes, fluoranthrenes anthrones, benzophenones, thioxanthones, anthracenes, and compounds containing carbon—carbon double bonds.

9. The composition of claim 1 wherein said crosslinking component comprises a glycoluril compound.

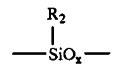
10. The composition of claim 1 wherein said composition consists essentially of components (a), (b), and (c).

11. The composition of claim 1 wherein polymer comprises one or more monomers selected from the group consisting of

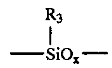
(I)



(II)



(III)



wherein x is from about 1 to about 1.5, R_1 is a chromophore moiety, R_2 is a transparent moiety, and R_3 is a reactive site for reaction with said crosslinking component.

* * * * *

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(19) United States

(12) Patent Application Publication

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Meador et al.

(54) THERMALLY CURABLE MIDDLE LAYER FOR 193-NM TRILAYER RESIST PROCESS

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(22) Filed: Feb. 20, 2004

Related U.S. Application Data

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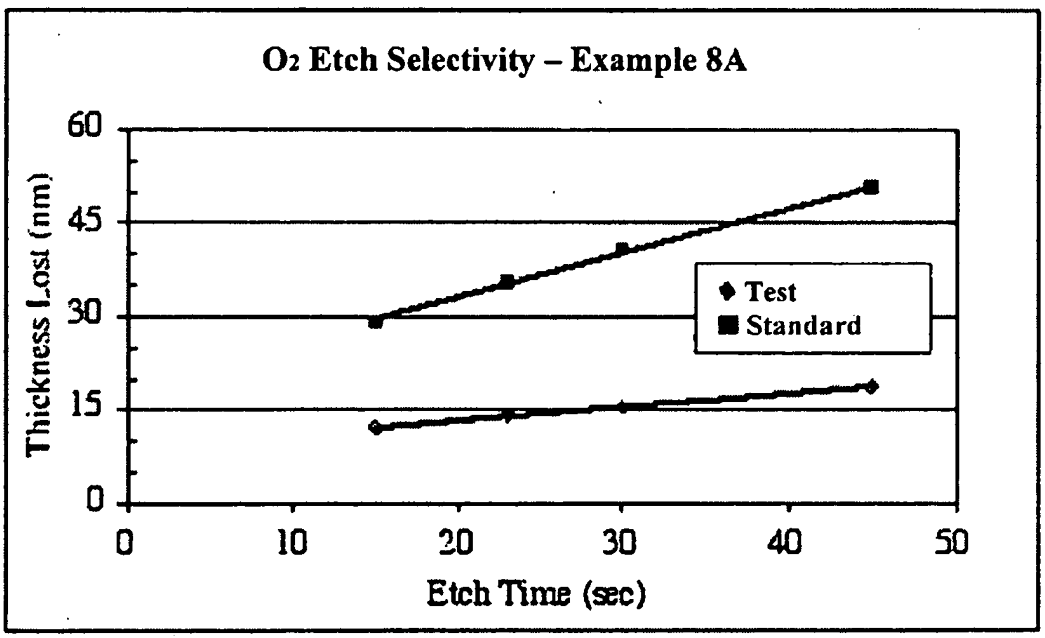
(52) U.S. Cl. 430/270.1

(57) ABSTRACT

New lithographic compositions (e.g., for use as middle layers in trilayer processes) are provided. In one embodiment, the compositions comprise an organo-silicon polymer dispersed or dissolved in a solvent system, and preferably a crosslinking agent and a catalyst. In another embodiment, the organo-silicon polymer is replaced with a polyhedral oligomeric silsesquioxane-containing polymer and/or a polyhedral oligomeric silsesquioxane. In either embodiment, the polymer and/or compound should also include —OH groups for proper cross-linking of the composition. When used as middle layers, these compositions can be applied as very thin films with a very thin layer of photoresist being applied to the top of the middle layer. Thus, the underlying bottom anti-reflective coating is still protected even though the overall stack (i.e., anti-reflective coating plus middle layer plus photoresist) is still thin compared to prior art stacks.



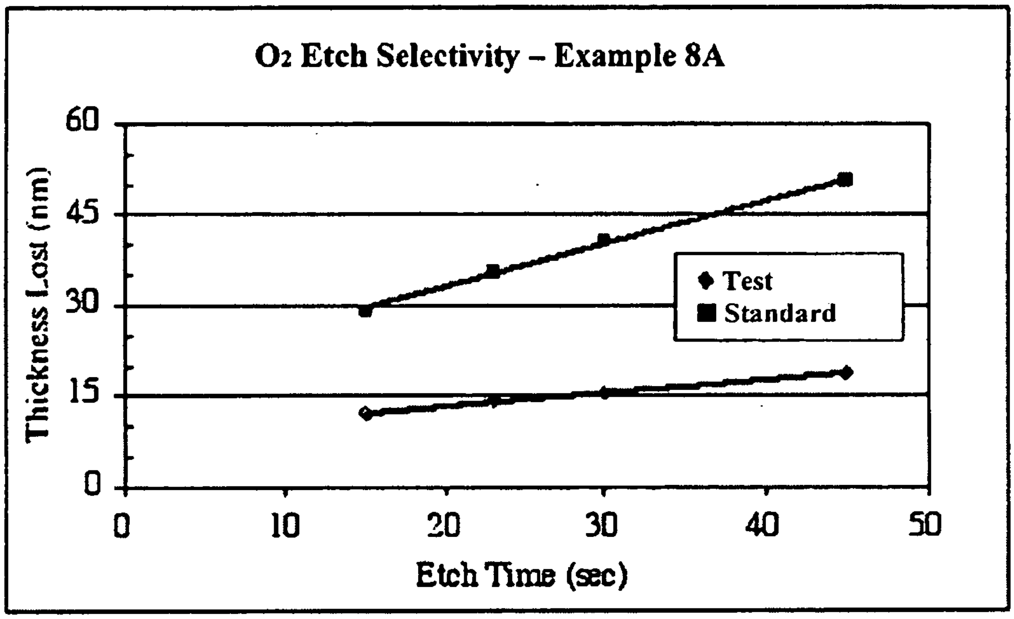

O_2 Etch Selectivity – Example 8A
Thickness Lost (nm)
60
45
30
15
0
0
10
20
30
40
50
Etch Time (sec)
Test
Standard

Fig. 1

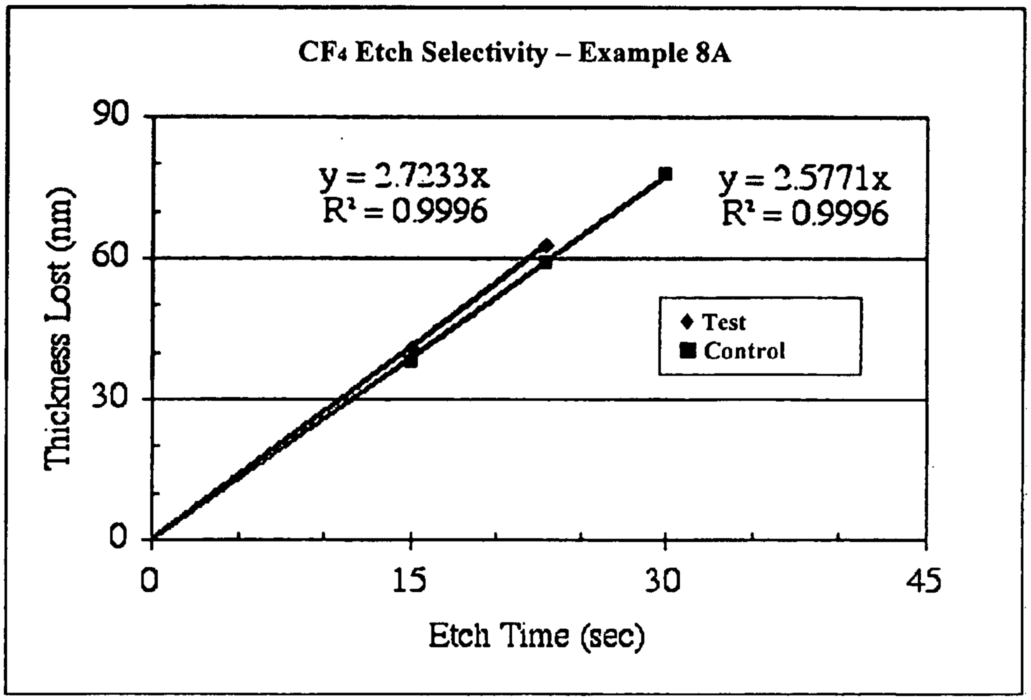

CF4 Etch Selectivity – Example 8A
y = 2.7233x
R² = 0.9996
y = 2.5771x
R² = 0.9996
Test
Control
Thickness Lost (nm)
Etch Time (sec)
90
60
30
0
0
15
30
45

Fig. 2

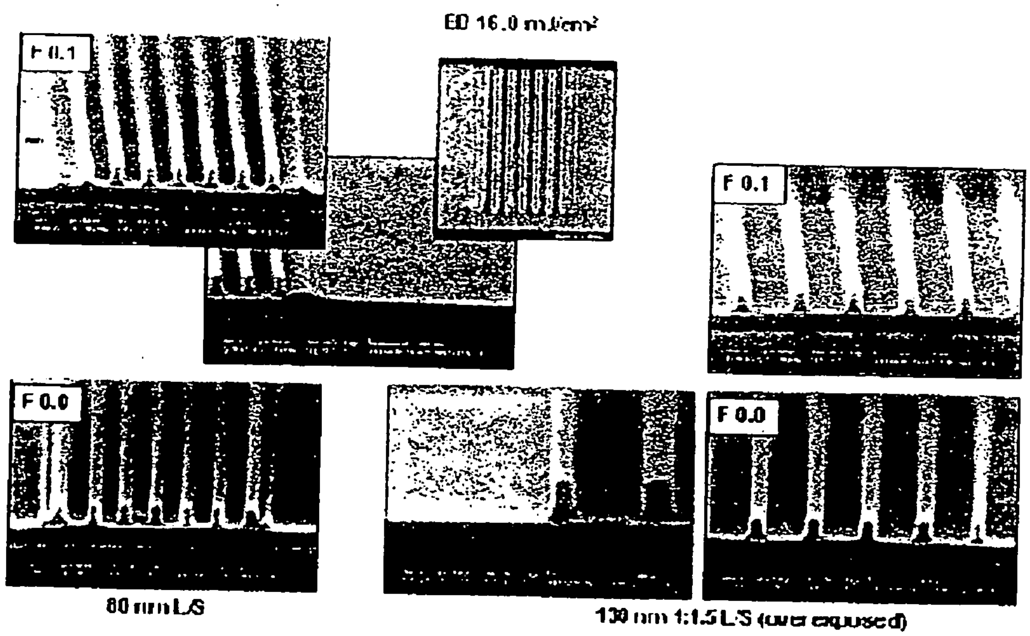


Fig. 3

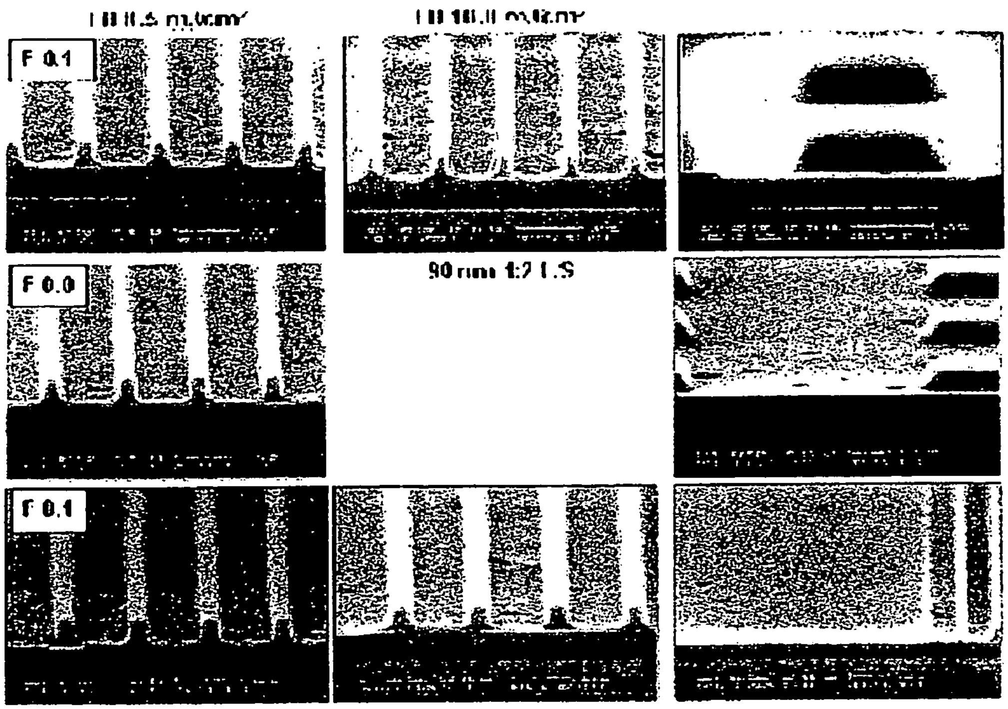


Fig. 4

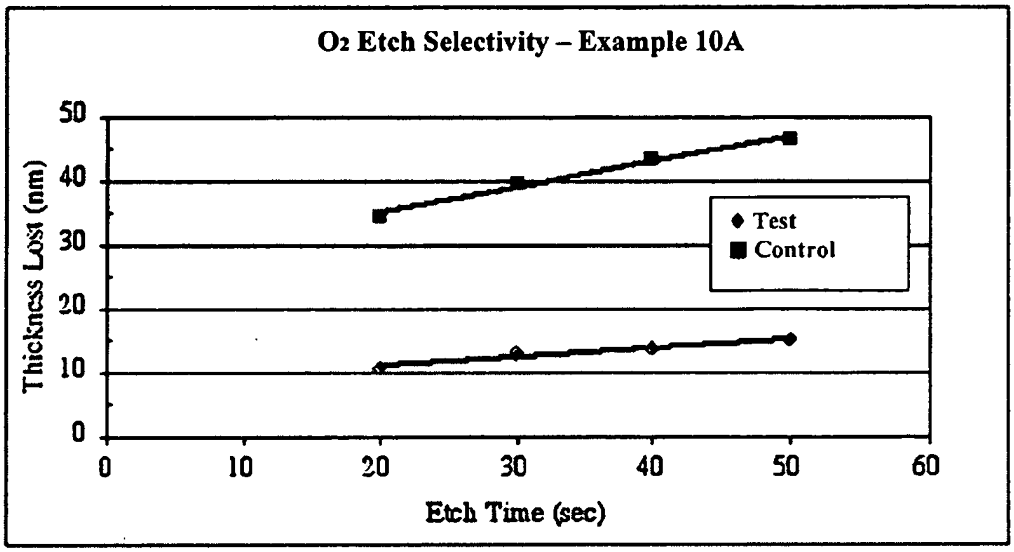

O2 Etch Selectivity – Example 10A
Thickness Lost (nm)
50
40
30
20
10
0
0
10
20
30
40
50
60
Etch Time (sec)
Test
Control

Fig. 5

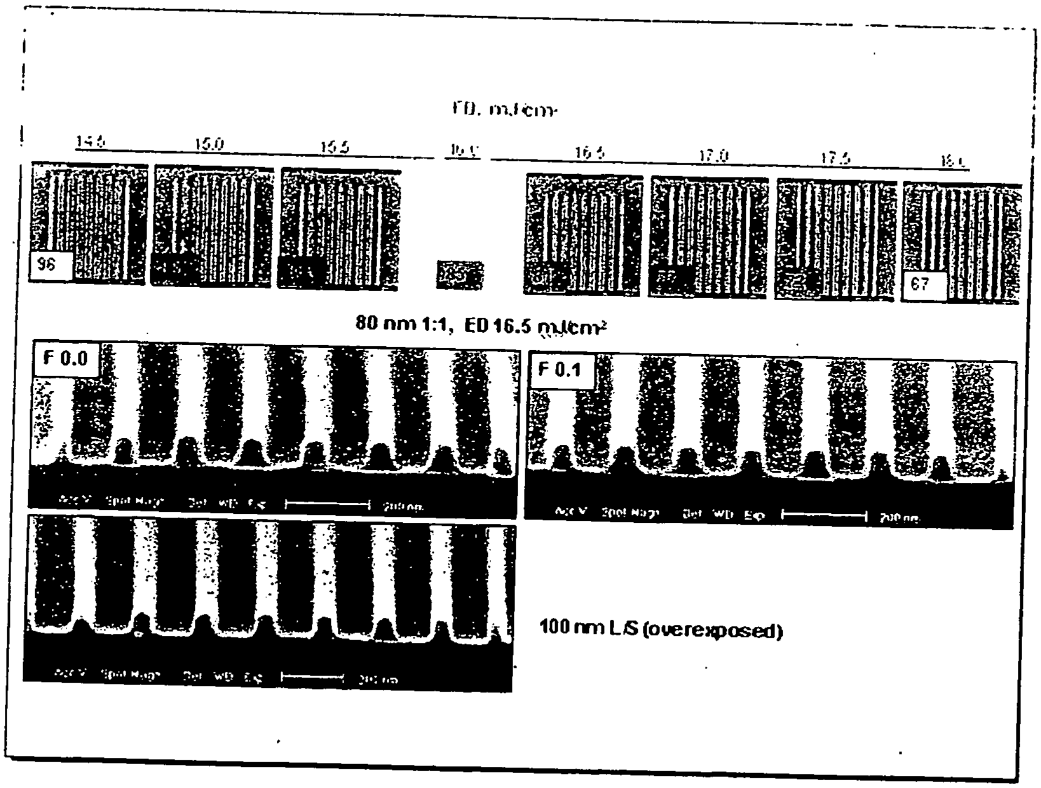


Fig. 6

THERMALLY CURABLE MIDDLE LAYER FOR 193-NM TRILAYER RESIST PROCESS

RELATED APPLICATIONS

[0001] This application claims the priority benefit of a provisional application entitled THERMALLY CURABLE MIDDLE LAYER FOR 193-NM TRILAYER RESIST PROCESS, Ser. No. 60/449,898, filed Feb. 24, 2003, incorporated by reference herein.

FEDERALLY SPONSORED RESEARCH/DEVELOPMENT PROGRAM

[0002] This invention was made with Government support under contracts DASG60-00-C-0044 and DASG60-01-0047, awarded by the United States Army Space and Missile Defense Command. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] The present invention is broadly concerned with new compositions for use as middle layers in trilayer resist processes. The compositions include an organo-silicon polymer or a polyhedral oligomeric silsesquioxane-containing polymer or compound dissolved in a solvent system.

[0005] 2. Description of the Prior Art

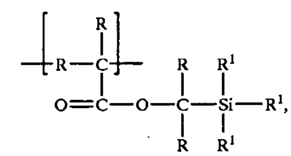
[0006] In order to store ever-increasing amounts of information on a substrate area, the microchip industry continues to move to shorter and shorter wavelengths of light for resist exposures. This trend towards decreasing linewidths leads to high aspect ratio lines, with the thin, tall lines tending to fall over during resist development/rinse steps. For 193-nm exposures, the microchip industry typically uses roughly 270-350 nm of resist on 32-80 nm of bottom anti-reflective coating—so-called unilayer processing. For trilayer applications, photoresist thicknesses (~150-200 nm) are much less than for unilayer applications, resulting in low aspect ratio lines. The trilayer bottom anti-reflective coating instead is 300-700 nm thick, and the middle layer is 30-215 (preferably 30-60) nm thick. The advantages of the trilayer resist processing include: (a) reduced resist aspect ratios; (b) the ability to use conventional or ultra-thin 193-nm photoresists rather than silicon-containing and hydrophobic (bilayer) resists; (c) minimized interaction of resist with the substrate; (d) optimum thickness control for the imaging, masking, and anti-reflective layer; and (e) improved depth-of-focus (DOF) since the trilayer bottom anti-reflective coatings are designed to be highly planarizing.

[0007] The key to trilayer imaging is a robust middle layer offering facile spin-applied processing, acceptable bottom anti-reflective coating/resist adhesion, excellent imageability, and outstanding etch selectivities to both bottom anti-reflective coating and resist. The middle layer must etch much slower than the bottom anti-reflective coating in an oxygen plasma and preferably faster than the photoresist in a fluorinated gas plasma. Prior approaches to the middle layer problem include the use of spin-on-glass, which requires careful attention to surface acidity in order to achieve acceptable adhesive properties.

SUMMARY OF THE INVENTION

[0008] The present invention is broadly concerned with new lithographic compositions and methods of using those compositions as middle or protective layers during circuit manufacturing.

[0009] In more detail, the compositions comprise a polymer or compound dispersed or dissolved in a solvent system. In one embodiment, that polymer is an organo-silicon polymer, preferably including recurring monomers having the formula



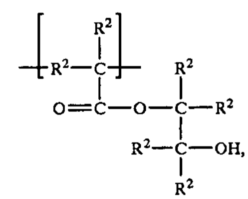
(I)

[0010] where:

[0011] each R is individually selected from the group consisting of hydrogen and alkyls (preferably C_1-C_6); and

[0012] each R^1 is individually selected from the group consisting of hydrogen, alkyls (preferably C_1-C_{12}, and more preferably C_1-C_6), and aryls (preferably C_6-C_{18}, and more preferably C_6-C_{12}).

[0013] The polymer of this embodiment preferably further comprises recurring monomers having an alcohol functionality. Preferred such monomers have the formula



(II)

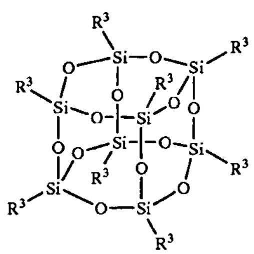
[0014] where each R^2 is individually selected from the group consisting of hydrogen, alkyls (preferably C_6-C_{12}, and more preferably C_1-C_6), and aryls (preferably C_6-C_{18}, and more preferably C_6-C_{12}).

[0015] The molar ratio of (I) to (II) is preferably from about 80:20 to about 50:50, and more preferably from about 75:25 to about 60:40. The weight average molecular weight of this polymer is preferably from about 35,000-100,000 Daltons, and more preferably from about 74,000-97,000 Daltons. Particularly preferred polymers according to this embodiment include copolymers of trimethylsilylmethyl methacrylate and hydroxypropyl methacrylate, although hydroxyethyl acrylate and/or hydroxy ethyl methacrylate could serve as the alcohol constituent as well.

[0016] In another embodiment, the composition will include a polymer having recurring monomers of a polyhedral oligomeric silsesquioxane such as those commercial-

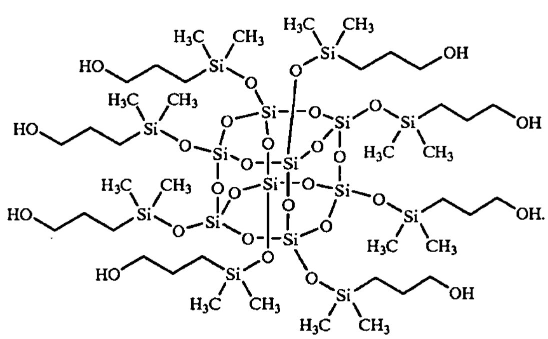
ized by Hybrid Plastics under the name POSS®, and/or the composition will include polyhedral oligomeric silsesquioxane compounds. One such compound (or monomer as the case may be) has the formula

(III)

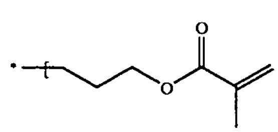


[0017] where each R^3 is individually selected from the group consisting of hydrogen, alkyls (preferably C_1-C_{12}, and more preferably C_1-C_6), aryls (preferably C_6-C_{18}, and more preferably C_6-C_{12}), hydroxypropyldimethylsilyloxy, and olefinic moieties.

[0018] One preferred (III) is a hydroxypropyldimethylsilyloxy compound having the. formula



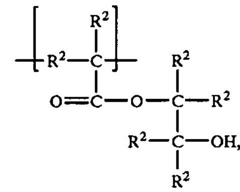
[0019] In embodiments where (III) is present as part of a polymer, the polymerization preferably takes place via an olefin group on R^3. Thus, at least one R^3 will include an olefinic moiety (such as in methacrylates or acrylates). In this embodiment, it is also preferred that at least one R^3 in (III) is



[0020] where "*" designates Si on (III).

[0021] As was the case with the organo-silicon polymer, it is preferred that the polymer or compound of this embodiment include alcohol functionality on the polyhedral oligomeric silsesquioxane and/or that the polymer further comprise recurring monomers having an alcohol functionality. One such preferred monomer has the formula

(IV)



[0022] where each R^2 is individually selected from the group consisting of hydrogen, alkyls (preferably C_1-C_{12}, and more preferably C_1-C_6), and aryls (preferably C_6-C_{18}, and more preferably C_6-C_{12}). The molar ratio of polyhedral oligomeric silsesquioxane to (IV) is preferably from about 15:85 to about 30:70, and more preferably from about 25:75 to about 20:80.

[0023] The inventive compositions generally have an overall solids content of from about 1.5-5.0% and can be prepared by simply dissolving or dispersing the polymer (and any other ingredients as discussed below) in a suitable solvent system. The solvent system should have a boiling point of from about 100-200° C., and preferably from about 120-170° C. The amount of polymer dissolved in the solvent system is from about 0.5-5.0% by weight polymer, preferably from about 1.0-4.0% by weight polymer, and more preferably from about 1.0-3.6% by weight polymer, based upon the total weight of the composition taken as 100% by weight.

[0024] The solvent system should be utilized at a level of from about 93-99.5% by weight, preferably from about 94-99% by weight, and more preferably from about 94-98.5% by weight, based upon the total weight of the composition taken as 100% by weight. Preferred solvent systems include a solvent selected from the group consisting of propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethyl lactate, propylene glycol n-propyl ether (PnP), cyclohexanone, tetrahydrofuran (THF), dimethyl formamide (DMF), γ-butyrolactone, 2-heptanone, N-methylpyrollidinone, and mixtures thereof.

[0025] Preferably, the inventive compositions further comprise a compound selected from the group consisting of crosslinking agents, catalysts, and mixtures thereof. Preferred crosslinking agents include those selected from the group consisting of aminoplast cross-linking agents (melamines, glycourils, etc., e.g., POWDERLINK 1174, Cymel® products). The crosslinking agent should be present in the composition at a level of from about 0.5-2.5% by weight, and preferably from about 0.5-1.5% by weight, based upon the total weight of the composition taken as 100% by weight. Thus, the compositions of the invention should crosslink at a temperature of from about 150-225° C., and more preferably from about 175-205° C.

[0026] Preferred catalysts include sulfonic acids (e.g., p-toluenesulfonic acid, styrene sulfonic acid), thermal acid generators (e.g., pyridinium tosylate), carboxylic acids (e.g., trichloroacetic acid, benzene tetracarboxylic acid), and mixtures thereof. The catalyst should be present in the compo-

sition at. a level of from about 0.1-1.0% by weight, and preferably from about 0.1-0.3% by weight, based upon the total weight of the composition taken as 100% by weight.

[0027] In a preferred embodiment, the compositions include a catalyst system comprising a weak acid as well as a low level of strong acid. Thus, the compositions would comprise less than about 1.0% by weight of a strong acid, preferably less than about 0.3% by weight of a strong acid, and more preferably less than about 0.1% by weight of a strong acid, based upon the total weight of the composition taken as 100% by weight. The weak acid would be present at a level of from about 0.02-1% by weight, more preferably from about 0.05-1% by weight, and even more preferably from about 0.05-0.5% by weight, based upon the total weight of the composition taken as 100% by weight. The weight ratio of strong acid to weak acid in the composition is from about 0:100 to about 50:50, preferably from about 5:95 to about 35:65, and more preferably about 2:98.

[0028] As used herein, the term "strong acid" is intended to refer to those compounds having a pK_a of less than about -6.0 at 25° C. Examples of strong acids include p-toluenesulfonic acid, sulfuric acid, hydrochloric acid, hydrobromic acid, nitric acid, trifluoroacetic acid, and perchloric acid. As used herein, the term "weak acid" is intended to refer to those compounds having a pK_a of greater than about 0, preferably from about 0-12, and more preferably from about 6-11 at 25° C. Preferred weak acids include phenolic compounds (including any phenolic compounds containing electron withdrawing groups, e.g., bis(4-hydroxyphenyl) sulfone or bisphenol S, bis(4-hydroxyphenyl) dimethylmethane or bisphenol A, α-cyano-4-hydroxycinnamic acid, phenol novolaks, benzenthiol, and phenols substituted with nitro groups, carbonyl groups, or carboxylic groups), carboxylic acids (e.g., acetic acid), and phosphoric acid.

[0029] The method of using the compositions simply comprises applying a quantity of a composition hereof to a surface by any conventional application method (including spincoating). For example, when used as a middle layer, the compositions would typically be applied to the top of a cured bottom anti-reflective coating, with the cured bottom anti-reflective coating being on a substrate. Exemplary substrates include Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

[0030] Cured compositions or middle layers according to the invention exhibit particularly good properties at wavelengths of less than about 400 nm (e.g., at 157-, 193-, and 248-nm wavelengths). For example, the cured compositions have an etch selectivity to resist (i.e., the middle layer etch rate divided by the photoresist etch rate) of at least about 1:1, and preferably at least about 1.2:1, when CF_4 is used as the etchant and 193-nm photoresists are used. The cured compositions have an etch selectivity to bottom anti-reflective coating of less than about 1:4, and preferably from about 1:11-1:31 when O_2 is used as the etchant and aromatic-containing bottom anti-reflective coatings are used.

[0031] Additionally, at 193- and 248-nm wavelengths, the cured layers have a k value (i.e., the imaginary component of the complex index of refraction) of less than about 0.5, and preferably less than about 0.08, and an n value (i.e., the real component of the complex index of refraction) of from about 1.4-1.8.

[0032] Furthermore, the cured layers according to the invention will be substantially insoluble in typical photoresist solvents. Thus, when subjected to a stripping test as defined herein, the cured layers will have a percent stripping of less than about 5%, preferably less than about 1%, and even more preferably about 0%. The stripping test involves first determining the thickness (by taking the average of measurements at five different locations) of a cured film. This is the average initial film thickness. Next, a solvent (e.g., ethyl lactate) is puddled onto the cured film for about 5 seconds, followed by spin drying at about 5,000 rpm for about 30 seconds to remove the solvent. The film thickness is measured again at five different points on the wafer using ellipsometry, and the average of these measuremnents is determined. This is the average final film thickness.

[0033] The amount of stripping is the difference between the initial and final average film thicknesses. The percent stripping is:

$$\%\ \text{stripping} = \left(\frac{\text{amount of stripping}}{\text{initial average film thickness}}\right) \times 100.$$

[0034] When the inventive compositions are subjected to a spin bowl compatibility test, they will achieve a result of at least about 90%, and preferably at least about 95% will be achieved. As used herein, the spin bowl compatibility is determined by coating a wafer with the composition. After coating, the wafers are not baked, but are instead placed in a wafer cassette. The coated surfaces are positioned upward in order to prevent film flow, and the samples are allowed to dry for about 24 hours in a cleanroom (ambient conditions) to yield films around 1300 Å thick. The sample thickness is measured on each wafer and is designated as the initial sample thickness.

[0035] The coated wafer is then exposed to a test solvent such as ethyl lactate or PGMEA. This is accomplished by centering a sample wafer on a spinner, followed by coating with the solvent evenly over the entire surface of the wafer. The sample is allowed to soak for 3 minutes followed by spinning dry for about 1 second at about 1500 rpm. After spinning, the thickness of the sample on the wafer is measured and designated as the final thickness.

[0036] The percent solubility is then calculated as follows:

$$\%\ \text{solubility} = \left[\frac{(\text{initial sample thickness} - \text{final sample thickness})}{(\text{initial sample thickness})}\right] * 100.$$

[0037] A photoresist can be applied to the cured material, followed by drying (soft bake), exposing, post-exposure baking, and developing the photoresist. Following the methods of the invention will yield precursor structures for use in trilayer processes, with the photoresist and middle layer in the "stacks" being relatively thin compared to prior art stacks. The cured bottom anti-reflective coating will typically have a thicknesses of from about 2,000-8,000 Å to ensure adequate etch resistance when transferring the photoresist patterns to the substrate. The cured inventive middle layers will have a thickness of less than about 2,150 Å, preferably less than about 1,000 Å, and more preferably

from about 300-600 Å. The dried photoresists will have a thickness of less than about 200 nm, preferably less than about 150 nm, and more preferably from about 60-150 nm. It will be appreciated that this is a significant advantage over prior art in that the imaging properties of the photoresist are present, and the bottom anti-reflective coating is protected even with a small stack size.

BRIEF DESCRIPTION OF THE DRAWINGS

[0038] FIG. 1 is a graph depicting the improved etch resistance of one of the inventive compositions when O_2 is used as the etchant;

[0039] FIG. 2 is a graph depicting the etch selectivity of one of the inventive compositions when CF_4 is used as the etchant;

[0040] FIG. 3 shows several scanning electron microscope (SEM) photographs containing respective cross-sectional views of wafers that have been processed with the inventive middle layers;

[0041] FIG. 4 shows several SEM photographs containing respective cross-sectional views of wafers that have been processed with the inventive middle layers;

[0042] FIG. 5 is a graph depicting the improved etch resistance of one of the inventive compositions when O_2 is used as the etchant; and

[0043] FIG. 6 shows several SEM photographs containing respective cross-sectional views of wafers that have been processed with the inventive middle layers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

EXAMPLES

[0044] The following examples set forth preferred methods in accordance with the invention. It is to be understood, however, that these examples are provided by way of illustration and nothing therein should be taken as a limitation upon the overall scope of the invention.

Example 1

Organo-Silicon Middle Layer

[0045] 1. Mother Liquor Synthesis

[0046] A 500-ml, three-necked flask equipped with magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 21.5 g (125 mmol) of trimethylsilylmethyl methacrylate, 15.2 g (105 mmol) of hydroxypropyl methacrylate, 148.0 g of PGMEA, and 367.0 mg of 2,2'-azobisisobutyronitrile (AIBN). The mixture was flushed with nitrogen for 15 minutes at ambient conditions, and the reaction flask then immersed into a heated oil bath. The polymerization solution was stirred under nitrogen at 72-74° C. solution temperature for 24 hours. After cooling to <35° C., about 46.2 mg of 4-methoxyphenol was added as an inhibitor, and the reaction product was stirred to homogeneity. The yield of copolymer solution was 98.2% of the theoretical yield. The weight-average molecular weight (Mw) for the copolymer by gel permeation chromatography (GPC) was 62,137.

[0047] 2. Formulation of Middle Layer

[0048] In this procedure, 38.5 g (21.9 meq polymeric hydroxyl) of the mother liquor prepared in Part 1 of this example, 249.0 g of PGMEA, 31.1 g of PnP, 2.35 g (21.9 meq) of POWDERLINK 1174 (an aminoplast crosslinking agent available from Cytec Industries), 97.6 mg of p-toluenesulfonic acid monohydrate (TSA), and 293.8 mg of bisphenol S were stirred to homogeneity at ambient conditions. About 16.1 g of PGME-washed 650C beads were added, and the mixture was tumbled for 4 hours at ambient conditions to effect deionization. The beads were removed by straining through two layers of plastic cloth, and the coating filtered twice through a 0.1 μm end-point filter.

[0049] 3. Film Properties

[0050] The coating prepared in Part 2 of this example was spin-coated onto a silicon wafer at 1500 rpm for 60 seconds and cured at 205° C. for 60 seconds using a hotplate under vacuum. The resulting middle layer film had a thickness of 79.5 nm. No smoking occurred during the hot plate bake, and the coating quality was very good. In an ethyl lactate thickness, stripping test to establish insolubility of the thermoset film in solvent, ethyl lactate was puddled on the film for 5 seconds and then spun off at 5000 rpm for 30 seconds. Film thickness was then re-measured. Stripping of ≦15 Å is considered acceptable. In the stripping test for this product, the film thickness increased by 3.51 Å (+0.32%). The film's 193-nm OD was 1.44/μm.

[0051] 4. Lithography

[0052] A trilayer stack comprised of a 330-nm thick layer of 193-nm photoresist (AR237J, available from JSR) on top of an 80-nm thick middle layer (as prepared in Part 2 of this example), on top of a 451-nm thick film of a bottom anti-reflective coating (see Part 2 of Example 2) gave excellent 0.11 μm semi-dense L/S with 0.4 μm depth-of-focus (DOF). Also, a trilayer stack including a 330-nm thick layer of AR237J on an 80-nm thick middle layer (prepared according to Part 2 of this example) on top of a 77-nm thick single layer anti-reflective coating (ARC29A-8, available from Brewer Science Inc., Rolla, Mo.) gave excellent 0.11 μm semi-dense L/S.

Example 2

Novolac Resin with Pendant Adamantane Function

[0053] 1. Preparation of Mother Liquor from Epoxy Novolac

[0054] A 500-ml, three-necked flask equipped with magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 25.0 g (142 meq epoxy) of an epoxy novolac (D.E.N. 431, available from Dow Chemical), 196.6 g of PnP, 24.36 g (135.2 mmol) of 1-adamantanecarboxylic acid, and 770 mg (3.38 mmol) of benzyltriethylammonium chloride. The mixture was flushed with nitrogen for 10 minutes at ambient conditions, and the reaction flask was then immersed in a heated oil bath. The reaction solution was stirred under nitrogen for 24.5 hours at 117.5-120° C. The yield of product was 244.8 g (99.2% of the theoretical yield).

[0055] 2. Formulation of Bottom Anti-Reflective Coating

[0056] About 120.0 g (65.7 meq polymeric hydroxyl function) of the mother liquor from Part 1 of this example, 31.6

g of PnP, 54.7 g of PGMEA, 7.42 g (69.0 meq) of POWDERLINK 1174, and 742.6 mg of TSA were stirred at ambient conditions to homogeneity. About 5 weight % (10.7 g) of PGME-washed 650C deionization beads were added, and the mixture was tumbled for 4 hours at ambient conditions to effect deionization. The beads were removed by straining through two layers of plastic cloth, and the bottom anti-reflective coating was then filtered twice through 0.1-μm end-point filters.

[0057] 3. Film Properties

[0058] The coating was spin-coated directly onto a silicon wafer at 1500 rpm for 60 seconds and cured at 205° C. for 60 seconds using a hot plate under vacuum. The resulting film had a thickness of 439.7 nm. Slight smoking occurred during the hot plate bake. The coating quality was good when assessed visually and under the microscope. Ethyl lactate thickness stripping was measured as only 5.3 Å (−0.12%). The cured bottom anti-reflective coating had a 193-nm optical density of about 10.5/μm.

[0059] 4. Optical Properties

[0060] The optical properties for the bottom anti-reflective coating prepared in Part 2 of this example were measured at 193-nm using a variable-angle spectroscopic ellipsometer (VASE) instrument. The n-value (real part of refractive index) was 1.6212, and the k-value (imaginary part of refractive index) was 0.3596.

[0061] 5. Prolith Modeling Reflectivity Back into the Resist

[0062] A trilayer stack using a 390-nm thick layer of photoresist (PAR-710, available from Sumitomo) on a 60.0-nm thick middle layer (prepared as described in Part 2, Example 5) on different thicknesses of the bottom anti-reflective coating prepared in Part 2 of this example was modeled on a silicon substrate using Prolith. The simulation results showed a straight line of slightly <0.8% reflectance back into the photoresist at all bottom anti-reflective coating thicknesses between 300 and 700 nm.

[0063] 6. Percent Planarity Over 200-nm Topography

[0064] At a coating thickness of approximately 451 nm, the bottom anti-reflective coating gave 74 to 90% planarity (1:1, 1:2, 1:4 L/S patterns) over 200-nm topography.

[0065] 7. Lithography

[0066] This testing was carried out as described in Part 4 of Example 1. A trilayer stack comprised of a 330-nm thick layer of 193-nm photoresist (AR237J), on top of an 80-nm thick middle layer (prepared as described in Part 2 of Example 1), on top of a 451-nm thick layer of a bottom anti-reflective coating (prepared in Part 2 of this example) was imaged and wet developed. SEM photos of cross-sections showed 0.11-μm semi-dense line spacing with 0.4-μm DOF. The lines were very rectangular in shape.

Example 3

Organo-Silicon Middle Layer

[0067] 1. Mother Liquor Synthesis

[0068] A 250-ml, three-necked flask equipped with magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 12.5 g (72.5 mmol) of trimethylsilylmethyl methacrylate, 5.65 g (39.2 mmol) of hydroxypropyl methacrylate, 103.6 g of PGMEA, and 0.183 g of AIBN. The mixture was purged with nitrogen at ambient conditions for 15 minutes and then stirred under nitrogen at 80-87° C. (primarily 84-86° C.) for 24 hours. After cooling to less than 40° C., 36.6 mg of 4-methoxyphenol inhibitor was added, and the solution was stirred to homogeneity. The yield of product was 92.8% of the theoretical yield. The Mw for the copolymer via GPC was 33,401.

[0069] 2. Formulation of Middle Layer

[0070] About 60.0 g (19.3 meq polymeric hydroxyl) of the mother liquor prepared in Part 1 of this example, 212.2 g of PGMEA, 2.28 g (21.2 meq) of POWDERLINK 1174, 93.9 mg of TSA, and 285.2 mg of bisphenol S were stirred to homogeneity at ambient conditions. Deionization was effected by adding 13.7 g of PGME-washed 650C deionization beads and tumbling at ambient conditions for 4 hours. The beads were subsequently removed by straining through two layers of plastic cloth, and the solution was filtered twice through a 0.1-μm end-point filter.

[0071] 3. Film Properties

[0072] The coating was spin-coated onto a silicon wafer at 1500 rpm for 60 seconds and cured at 205° C. for 60 seconds using a hot plate under vacuum. The resulting film had a thickness of 107.8 nm. No smoking occurred during the hot plate bake, and coating quality was good. In the ethyl lactate stripping test, the film swelled by +0.40%. The film's 193-nm OD was 1.23/μm.

[0073] 4. Optical Parameters

[0074] The optical constants for the coating were measured at 193 nm using a VASE instrument. The n-value was 1.694, and the k-value was 0.0403.

[0075] 5. Etch Selectivity

[0076] The O_2 etch selectivity of the middle layer to a multilayer bottom anti-reflective coating (DH2333-1-1, a bottom anti-reflective coating using an acrylic/9-anthraceneecarboxylic acid adduct binder polymer) on a Trion etcher was 1 to 6.4. On an NSC (ES401) etcher, the CF_4 etch selectivity of the middle layer to a 193-nm photoresist (PAR-710, available from Sumitomo) was 1.44. Using an Applied Materials etcher, the CF_4 etch selectivity was measured as 1.24.

[0077] 6. Lithography

[0078] A trilayer stack comprised of a 330-nm thick layer of 193-nm photoresist (AR237J) on top of a 108-nm thick middle layer prepared according to Part 2 of this example which was on top of a 77-nm thick, single layer bottom anti-reflective coating (ARC29A, available from Brewer Science Inc.) gave excellent 0.11-μm semi-dense line spacing with 0.3-μm DOF after wet development.

Example 4

Novolac Resin with Pendent Adamantane Function

[0079] 1. Mother Liquor Synthesis

[0080] A 500-ml three-necked flask equipped with a magnetic stirring bar, thermometer, nitrogen inlet, and condenser

with nitrogen outlet was charged with 25.0 g (140 meq epoxy) of D.E.N. 438, 276.8 g of PGME, 23.98 g (133.0 mmol) of 1-adamantanecarboxylic acid, and 0.759 g (3.33 mmol) of benzyltriethylammonium chloride. The mixture was gently flushed with nitrogen for 10 minutes at ambient conditions and then immersed in a heated oil bath. The reaction solution was heated under nitrogen at 115° C. for 24 hours.

[0081] 2. Formulation of Bottom Anti-Reflective Coating

[0082] About 125.0 g (50.9 meq of polymeric hydroxyl) of the mother liquor prepared in Part 1 of this example, 45.6 g of PGMEA, and 4.38 g (40.8 meq) of POWDERLINK 1174 were stirred to homogeneity at ambient conditions. The resulting solution was deionized by tumbling with 8.75 g of PGME-washed 650C beads for 4 hours. The beads were removed by straining through two layers of plastic cloth. The deionized solution was then filtered twice through a 0.20/0.45-μm end-point filter into a tared Nalgene bottle. About 758 mg of pyridinium tosylate were added per 175.0 g of filtrate. The product (now containing catalyst) was stirred to homogeneity and twice filtered through a 0.1-μm end-point filter.

[0083] 3. Film Properties

[0084] The bottom anti-reflective coating prepared in Part 2 of this example was spin-coated onto a silicon wafer at 1500 rpm for 60 seconds, followed by a cure at 205° C. for 60 seconds under a hot plate vacuum gave a thickness of 476-nm. The coating quality was good visually, but mottled (uneven) under the microscope. In the ethyl lactate stripping test, the film thickness decreased by 0.35%. The cured film's 193-nm OD was about 10.1-11.4/μm.

[0085] 4. Optical Parameters

[0086] As measured at 193 nm using a VASE, the n-value for the bottom anti-reflective coating prepared in Part 2 of this example was 1.62, and the k-value was 0.34.

[0087] 5. Etch Selectivity

[0088] Using an Applied Materials etcher, the etch selectivity of this bottom anti-reflective coating to Sumitomo's PAR-710 resist was 0.946 with an O_2- plasma, and 0.954 with a CF_4-plasma.

[0089] 6. Percent Planarity Over 200-nm Topography

[0090] At a coating thickness of about 475-nm, the coating gave 84-94% planarity (1:1, 1:2, 1:4 L/S) over 200-nm topography.

[0091] 7. Spin Bowl Compatibility

[0092] A rapid re-dissolution of a dried bottom anti-reflective coating in coating solvents is considered essential to prevent build-up of polymer on the walls of the spin bowl and to avoid the need for an unwanted bowl cleaning step. If at least about 90% of the dried coating re-dissolves during the test, the product is considered spin bowl compatible. This coating exhibited completely satisfactory spin bowl compatibilities that varied between 97.6-99.5% for six different solvents (acetone, cyclohexanone, 2-heptanone, ethyl lactate, PGME, and PGMEA).

[0093] 8. Resist Interlayer

[0094] Any intermixing of photoresist with cured anti-reflective coating during application of the photoresist may result in footing or slope at the base of resist features. To quantitatively measure intermixing, a photoresist interlayer test is run by: (1) applying and curing the coating on a silicon substrate; (2) measuring the coating thickness; (3) applying a resist onto the coating; (4) drying, exposing, and post-exposure baking the resist; (5) developing the resist; (6) water rinsing the wafer followed by drying; (7) re-measuring the coating thickness; and (8) calculating the change in coating thickness. Using Sumitomo's AX4846A-25 as the resist gave 48 Å for the interlayer for the coating in Part 2 of this example. An interlayer value of less than about 50 Å is considered acceptable.

[0095] 9. Lithography

[0096] This product was not tested in a trilayer imaging configuration. However, using this coating as a thick (477-nm) bottom anti-reflective coating under JSR's 193-nm resist AR237J (model bilayer configuration) gave standing 0.12-μm, semi-dense L/S. The DOF was extremely narrow (ca. 0.2 μm), and an interaction layer between the resist and coating was clearly visible.

Example 5

Organo-Silicon Middle Layer

[0097] 1. Mother Liquor Synthesis

[0098] A 500-ml three-necked flask equipped with a magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 18.04 g (104.7 mmol) of trimethylsilylmethyl methacrylate (Gelest, product number SIM6485.6), 8.15 g (56.4 mmol) of hydroxypropyl methacrylate (Aldrich, product number 26,854-2), 149.5 g of PGMEA, and 261.9 mg of AIBN. The polymerization mixture was purged with nitrogen for 16 minutes at ambient conditions, and the reaction flask then immersed in a heated oil bath. The reaction was stirred under nitrogen atmosphere for 24 hours at a solution temperature of 69-74.5° C. After the solution was cooled to 34° C., 44.4 mg of 4-methoxyphenol was added as an inhibitor. This solution was then stirred to homogeneity. The weight of the product was 98% of the theoretical yield. The weight-average molecular weight (Mw) for this copolymer was 74,073.

[0099] 2. Formulation of Middle Layer

[0100] The following ingredients were added to a 1-liter Nalgene bottle in the stated order: 60.0 g (19.2 meq polymeric hydroxyl) of the mother liquor prepared in Part 1 of this example, 287.3 g of PGMEA, 2.28 g (21.2 meq) of POWDERLINK 1174,93.9 mg of TSA, and 285.2 mg of bisphenol S. The mixture was stirred to homogeneity at ambient conditions, followed by a 4-hour tumble with 5 weight % of PGME-washed 650C deionization beads. The beads were removed by straining through two layers of plastic cloth. The coating was then filtered twice through a 0.1-μm end-point filter.

[0101] 3. Film Properties

[0102] The composition prepared in Part 2 of this example was spin-coated directly onto a silicon wafer at 1500 rpm for 60 seconds and cured at 205° C. for 60 seconds on a hot plate

under vacuum. The result was 86.4 nm of cured film. Smoke was not observed during the hot plate bake step, and coating quality was good. In the ethyl lactate stripping test, the film increased (swelled) in thickness by +0.52% (4 to 5 Å). The 193-nm optical density (OD) of the silicon-containing film was only 1.10/μm.

[0103] 4. Optical Parameters

[0104] As measured at 193 nm by a VASE, the n-value for this coating was 1.691, and the k-value was 0.0396.

[0105] 5. Etch Selectivity

[0106] The etch selectivity of this coating to PAR-710 using an NSC etcher (model ES401) and a CF_4-plasma was 1.50.

Example 6

Novolac Resin with Pendent Adamantane Function

[0107] 1. Preparation of Mother Liquor

[0108] A 500-ml three-necked flask equipped with magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 25.0 g (140 meq epoxy) of D.E.N. 438, 196.2 g of PGMEA, 24.0 g (133 mmol) of 1-adamantanecarboxylic acid, and 758.8 mg (3.33 mmol) of benzyltriethylammonium chloride. The mixture was gently purged with nitrogen for 15 minutes at ambient conditions and then immersed in an oil, bath. The reaction solution was heated under nitrogen at 113-119° C. (primarily 113° C.) for 24 hours. The yield of product was 98.3% of the theoretical yield.

[0109] 2. Formulation of Bottom Anti-Reflective Coating

[0110] About 120.0 g (64.9 meq polymeric hydroxyl) of mother liquor prepared in Part 1 of this example, 85.9 g of PGMEA, 7.36 g (68.5 mmol) of POWDERLINK 1174, and. 736.3 mg of TSA were stirred at ambient conditions to give a solution. Deionization was effected by adding 10.7 g of PGME-washed 650C beads and tumbling for 4 hours. The beads were removed by straining through two layers of plastic cloth and the solution then filtered through a 0.1-μm end-point filter.

[0111] 3. Film Properties

[0112] The coating prepared in Part 2 of this example was spin-coated onto a silicon wafer at 1500 rpm for 60 seconds and cured at 205° C. for 60 seconds under hotplate vacuum. The film thickness was 4142 Å. The coating quality was good, but 25 considerable smoke evolved during the hot plate bake. In the ethyl lactate stripping test, 4.5 Å (−0.11%) of cured film was lost. The film's OD at 193 nm was 9.21/μm.

[0113] 4. Interlayer Test

[0114] This test was described under Part 8 of Example 4. The measured interlayer for this coating using Sumitomo's AR4846A25 as the resist was 134 Å.

[0115] 5. Lithography

[0116] A trilayer configuration of JSR's AR237J on top of a middle layer as prepared in Part 2 of Example 5, on top of a coating as prepared in Part 2 of this example was imaged and yielded 100-nm, semi-dense L/S with a 0.5 μm DOF.

Example 7

[0117] 1. Mother Liquor Synthesis

[0118] A 250-ml, three-necked flask equipped with a magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 5.0 g (39.5 mmol) of methacryloxymethylphenyldimethylsilane [Gelest, SIM6481.5], 1.65 g (11.4 mmol) of hydroxypropyl methacrylate, 60.3 g of PGMEA, and 66.3 mg of AIBN. The mixture was flushed with nitrogen for 15 minutes at ambient conditions, and the flask then immersed in an oil bath. Stirring under a nitrogen atmosphere, the polymerization solution temperature was maintained at 70-71 ° C. for 23 hours. After cooling to <35° C., about 11.9 mg of 4-methoxyphenol was added as inhibitor, followed by stirring to homogeneity overnight. The weight of product was 98% of the theoretical yield.

[0119] 2. Formulation of the Middle Layer

[0120] About 60.4 g of the mother liquor prepared in Part 1 of this example, 77.1 g of PnP, and 0.77 g of POWDERLINK 1174 were stirred at ambient conditions to homogeneity. About 6.9 g of deionization beads were added, and the mixture was tumbled for 4 hours at ambient conditions. The beads were removed by straining through 2 layers of plastic cloth, and the coating filtered twice through a 0.1 μm end-point filter. Pyridinium tosylate (0.097 weight % of filtrate) was added, and the mixture was stirred to homogeneity and filtered once through a 0.1 μm end-point filter.

[0121] 3. Film Properties

[0122] The middle layer composition prepared in Part 2 of this example was spin-coated directly onto a silicon wafer at 1500 rpm for 60 seconds and cured at 205° C. for 60 seconds with a hotplate vacuum to yield a cured film having a thickness of 1315 Å. Very slight smoking on the hotplate was observed during curing. The film had a good coat quality. The ethyl lactate film thickness stripping was −0.08%, and 193-nm OD of the layer was 13.2/μm.

[0123] 4. Lithography

[0124] This middle layer composition was spun/cured directly onto a silicon wafer to yield a film having a thickness of 136.4 nm. A photoresist (AR237J) was coated/dried to a thickness of 330 nm on the middle layer. After exposure/processing, SEM photos showed 0.11-μm, semi-dense L/S with some footing at the base of lines and a thin resist interaction layer.

Example 8A

[0125] 1. Mother Liquor Synthesis from MethacrylEthyl Polyhedral Oligomeric Silsesquioxane

[0126] A 100-ml three-necked flask equipped with magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 4.00 g (5.35 mmol) of methacrylethyl polyhedral oligomeric silsesquioxane, 2.67 g (18.52 mmol) of hydroxypropyl methacrylate), 60.7 g of PGMEA, and 66.6 mg of AIBN. The mixture was polymerized under a nitrogen blanket for 24 hours at 60.5-63° C. After the solution cooled to 26.5° C., 17.1 mg of 4-methoxyphenol was added as an inhibitor. Stirring to homogeneity, the weight of product was 98.7% of the theoretical

yield. The weight-average molecular weight of this copolymer as determined by GPC was 55,700.

[0127] 2. Formulation of the Corresponding Middle Layer

[0128] The following ingredients were added to a 250 ml Nalgene bottle in the stated order: 30.0 g of the mother liquor prepared in Part 1 of this example, 89.8 g of PGMEA, 886 mg of POWDERLINK 1174, 36.8 mg TSA, and 110.6 mg of 4,4'-sulfonyldiphenol. The mixture was stirred to homogeneity at ambient conditions, followed by a 4-hour tumble with 6.0 g of PGME-washed 650C deionization beads. The beads were removed by straining through two layers of plastic cloth, and the middle layer was then filtered twice through a 0.1 μm end-point filter.

[0129] 3. Film Properties

[0130] The middle layer was spun directly onto silicon wafers at 1250 rpm for 60 seconds followed by curing at 205° C. for 60 seconds with hotplate vacuum to yield a film having a thickness of 736.1 Å. A trace of smoking was visible during the hotplate bake. The ethyl lactate thickness stripping was +0.43% (i.e., a slight swell). Spinning/curing onto quartz wafers using identical conditions gave a 193-nm OD of 1.6.

[0131] 4. Optical Parameters

[0132] A VASE was used to measure the real part of the refractive index (n) and the imaginary part of the refractive index (k) for the cured film. The 193-nm n and k values were 1.66 and 0.059, respectively.

[0133] 5. Plasma Etching the Cured Film on a Silicon Substrate

[0134] Using a Trion etcher, the middle layer of Part 2 of this example and the a control or standard middle layer (EML DH2333-29, a middle layer having alkyl silane) were etched with: a) O_2 and b) CF_4. The results are shown in **FIGS. 1 and 2**, with the layer of-Part 2 of this example etching much slower than the alkyl silane standard in O_2, but at a selectivity of about 1.1 in CF_4.

[0135] 6. Trilayer Lithography

[0136] A trilayer configuration was formed of ARC29A-8 (thickness of 77 nm, available from Brewer Science Inc.) topped with a 73.6-nm thick layer of the middle layer formed in Part 2 of this example with a thin layer (200 nm) of the resist, GARS8107A10 (available from Arch Chemical). Exposure and wet processing yielded 80-nm dense, 1:1, L/S, with some line footing and a small amount of scum between the lines. The SEM data is shown in **FIG. 3**.

[0137] A trilayer stack comprised of a thin layer of the resist, GARS8207K21 (thickness of 150 nm, available from Arch Chemical), on top of a 73.6-nm thick layer of the middle layer from Part 2 of this example, on top of a thin layer (77 nm) of ARC29A-8 was exposed and wet-processed to yield 90-nm, 1:2 L/S. The SEM data is shown in **FIG. 4**.

[0138] 7. Spin Bowl Compatibility

[0139] The middle layer of Part 2 of this example was tested for re-dissolving or spin bowl performance using the procedure described previously. About 52-82% of the dried films re-dissolved. The solvents were acetone, cyclohexanone, 2-heptanone, ethyl lactate, PGME, and PGMEA. This was below the specified passing value of 2 90% re-dissolution.

Example 8B

[0140] 1. Formulation of Middle Layer

[0141] The following ingredients were stirred at ambient conditions to give a solution: the mother liquor prepared in Part 1 of Example 8A (28.0 g), PGMEA (43.5 g), PGME (11.2 g), POWDERLINK 1174 (413.3 mg), bisphenol A (104.2 mg), TSA (6.0 mg), and CYMEL 303LF (17.3 mg). About 4.2 g of PGME-washed 650C beads were added, the mixture tumbled for 4 hr to effect deionization, and the beads then removed by straining through two layers of plastic cloth. The middle layer composition was then filtered through a 0.1 μm end-point filter.

[0142] 2. Film Properties

[0143] The middle layer composition prepared in Part 1 of this example was spin-coated onto silicon wafers at 1500 rpm for 60 seconds followed by a cure at 205° C. for 60 seconds with hotplate vacuum to yield a film thickness of 884.6 Å. A spin/cure process onto quartz wafers using identical conditions gave a 193-nm optical density of 0.95. Coat quality was good both visually and under the microscope. The ethyl lactate stripping test resulted in a +0.85% increase in film thickness, i.e., film swelling rather than film loss.

[0144] 3. Optical Parameters

[0145] Using the VASE, the n and k values of the cured film were 1.646 and 0.025, respectively, at 193 nm.

[0146] 4. Spin Bowl Compatibility

[0147] The re-dissolution performance of this layer was measured using the spin bowl compatibility test described previously. The following solvents were used in this test: acetone, cyclohexanone, 2-heptanone, ethyl lactate, PGME, and PGMEA. About 96.1-97.5% of the film re-dissolved, showing the product to be highly spin bowl compatible, thus differing from the film prepared in Example 8A.

Example 9

[0148] 1. Mother Liquor Synthesis Using Methacryllsobutyl Polyhedral Oligomeric Silsesquioxane

[0149] A 250-ml, three-necked flask equipped with a magnetic stirring bar, thermometer, nitrogen inlet, and condenser with nitrogen outlet was charged with 2.67 g (18.5 mmol) of hydroxypropyl methacrylate, 70.28 g of PGMEA, 5.05 g (5.35 mmol) of methacrylisobutyl polyhedral oligomeric silsesquioxane, and 77.3 mg of AIBN. The mixture was flushed with nitrogen for 15 minutes at ambient conditions, and the flask was immersed in an oil bath at 66° C. The reaction solution was stirred under a nitrogen blanket for 24 hours at 64-65.5° C. With the reaction solution temperature <26° C., about 19.6 mg of 4-methoxyphenol was then added as an inhibitor. The mixture was stirred to homogeneity at ambient conditions, with the yield being 75.3 g (96.4% recovery). The Mw for the copolymer via GPC analysis was 56,500. In addition to the copolymer, there was a minor peak in the GPC scan with a Mw of 764

that may have corresponded to unreacted methacrylisobutyl polyhedral oligomeric silsesquioxane.

[0150] 2. Formulation of Middle Layer

[0151] The following ingredients were stirred at ambient conditions to form a middle layer composition: the mother liquor prepared in Part 1 of this example (32.0 g), PGMEA (48.1 g), PGME (12.5 g), POWDERLINK 1174 (408.1 mg), bisphenol A (102.6 mg), TSA (6.0 mg), and CYMEL 303LF (17.2 mg). The solution was deionized by tumbling with 5 weight % of PGME-washed 650C beads for 4 hr. The beads were removed by straining through two layers of plastic cloth, and the middle layer was then filtered twice through a single 0.1 μm end-point.

[0152] 3. Film Properties

[0153] The middle layer prepared in Part 2 of this example was spin applied to silicon wafers at 1000 rpm for 60 seconds and cured at 205° C. for 60 seconds with hotplate vacuum. The film thickness was 1148.11 Å. A moderate amount of smoke evolved during the hotplate bake step. Coat quality was excellent, both visually and under the microscope. Ethyl lactate stripping resulted in +0.28% change in the cured film thickness.

[0154] Using identical spin/cure conditions, the hardmask was then applied to quartz wafers. The 193-nm absorbance was very low (+0.075), with the OD then being only 0.65.

[0155] 4. Spin Bowl Compatibility

[0156] This CYMEL 303LF-containing middle layer composition was 94% (composite score) spin bowl compatible using the following different solvents: acetone, cyclohexanone, 2-heptanone, PGME, ethyl lactate, and PGMEA.

Example 10A

[0157] 1. Formulation of Middle Layer from Octahydroxypropyldimethylsilyl Polyhedral Oligomeric Silsesquioxane

[0158] A 125-ml Nalgene bottle was charged with 1.526 g (8.24 mmol hydroxyl function) of octahydroxypropyldimethylsilyl polyhedral oligomeric silsesquioxane, 67.3 g of PGMEA, 660.5 mg (6.14 meq) of POWDERLINK 1174, 27.4 mg TSA, and 82.3 mg of 4,4'-sulfonyldiphenol. The mixture was stirred at ambient conditions giving a solution. About 3.5 g of PGME-washed 650C beads were added, and the mixture was tumbled for 4 hours at ambient conditions to remove cations. The beads were removed by straining through two layers of plastic cloth. The middle layer composition was then filtered twice through a 0.1-μm end-point filter.

[0159] 2. Film Properties

[0160] Spin application onto silicon wafers was at 1000 rpm for 60 seconds, with curing being carried out at 205° C. for 60 seconds with hotplate vacuum. The film thickness was 657.7 Å. There was no smoking during the hotplate bake. Coat quality, both visually and under the microscope, was good. Ethyl lactate stripping was +0.09%. Application/cure on quartz wafers using identical conditions gave a 193-nm absorbance of 0.129 and a 193-nm OD of 1.96.

[0161] 3. Optical Parameters

[0162] The VASE was used to measure the 193-nm n and k values for cured film, with the respective numbers being 1.677 and 0.0669.

[0163] 4. Spin Bowl Compatibility

[0164] This property was checked using seven different solvents: acetone, cyclohexanone, 2-heptanone, PGME, ethyl lactate, PGMEA, and 1-methyl-2-pyrrolidinone. The percent re-dissolution varied between 9.7% and 11.0%. The middle layer composition was not spin bowl compatible.

[0165] 5. Plasma Etching the Cured Film on a Silicon Substrate

[0166] Using a Trion etcher with O_2 as the etching gas, the middle layer prepared in Part 2 of this example etched about 68.6% slower than the alkyl silane standard (hard mask DH2333-29), i.e., the etch selectivity for the former relative to the latter was 0.30-0.32. The data is shown in **FIG. 5**.

[0167] 6. Trilayer Lithography

[0168] A trilayer stack comprised of a thin layer (200 nm) of resist (GARS8107A10) on top of a 658-Å layer of the middle layer prepared in Part 1 of this example, on top of a bottom anti-reflective coating (BAKC DH2333-42, a bottom anti-reflective coating with the binder material being an aliphatic triepoxy/(9-anthracenecarboxylic acid:1-adamantane carboxylic acid (1/1 mole)) adduct) was 193-nm imaged and then processed. The SEM photos of cross-sections showed 80-nm, 1:1 L/S, with a small amount of scum between the lines. The data is shown in **FIG. 7**.

Example 10B

[0169] 1. Formulation of Middle Layer

[0170] About 1.384 g (7.47 mmol hydroxyl) of octahydroxypropyldimethylsilyl polyhedral oligomeric silsesquioxane, 61.0 g of PGMEA, 402.1 mg of POWDERLINK 1174, 100.5 mg of bisphenol A, 5.9 mg TSA, and 16.8 mg of CYMEL 303LF were stirred to give a solution. The solution was deionized by tumbling with 3.1 g of PGME-washed 650C beads for 4 hours. The beads were removed by straining through two layers of plastic cloth. The middle layer composition was then twice filtered through a 0.1-μm end-point filter.

[0171] 2. Film Properties

[0172] The composition was spin-coated at 850 rpm for 60 seconds onto silicon wafers and cured at 205° C. for 60 seconds with hotplate vacuum. Film thickness was 614 Å, with a slight amount of smoke noted during the hotplate bake. Visual coat quality was excellent, but under the microscope many dark pinpoints were observed. Ethyl lactate stripping was +0.31%, i.e., slight swelling. Under the microscope, the stripped wafer still showed the pinpoint defects. Application/cure on quartz wafers, under identical conditions gave a 193-nm OD of 2.3.

[0173] 3. Spin Bowl Compatibility

[0174] Spin bowl compatibility testing was carried out with the following six solvents: PGMEA, cyclohexanone, ethyl lactate, acetone, 2-heptanone, and PGME. Re-dissolution of the dried film varied between 95% and 98%. Thus, this CYMEL 303LF-containing middle layer variant was highly spin bowl compatible.

[0175] 4. Plasma Etching the Cured Film on a Silicon Substrate

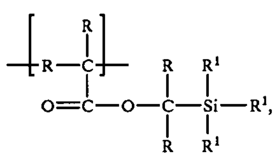
[0176] Using a Trion etcher with O_2 as the etching gas, the middle layer prepared in Part 2 of this example etched at about one quarter of the speed of the alkyl silane standard (hard mask DH2333-29). Etching selectivity to the bottom anti-reflective coating (described in Example 10A) in an O_2 plasma was 1:31.5. Using CF_4 as the etching gas in the same etcher gave a selectivity of 1:1.

[0177] 5. Trilayer Lithography

[0178] A trilayer stack comprised of a thin layer (200 nm) of resist (GARS8107A10) on top of a 630-Å layer of the middle layer prepared in Part 1 of this example, on top of a bottom anti-reflective coating (with the binder material being an aliphatic, multi-functional epoxy/9-anthracenecarboxylic acid adduct) was 193-nm imaged and then processed. The SEM photo of the cross-sections showed 80-nm, 1:1 L/S, with a 0.6 μm DOF. The spaces between the lines were relatively clean.

We claim:

1. In a composition for use in microlithographic processes, wherein the composition comprises a polymer dissolved or dispersed in a solvent system, the improvement being that said polymer comprises recurring monomers having the formula



(I)

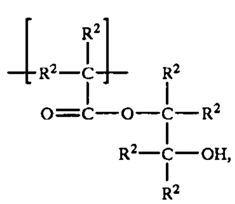
wherein:

each R is individually selected from the group consisting of hydrogen and alkyls; and

each R^1 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

2. The composition of claim 1, said polymer further comprising recurring monomers having an alcohol functionality.

3. The composition of claim 2, said polymer comprising recurring monomers having the formula



(II)

wherein each R^2 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

4. The composition of claim 3, wherein the molar ratio of (I) to (II) is from about 80:20 to about 50:50.

5. The composition of claim 1, said composition further comprising a cross-linking agent.

6. The composition of claim 5, wherein said cross-linking agent is selected from the group consisting of aminoplast cross-linking agents.

7. The composition of claim 5, said composition further comprising a catalyst.

8. The composition of claim 7, wherein said catalyst is an acid.

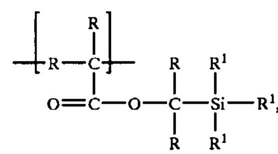
9. The composition of claim 8, wherein said composition comprises a weak acid and a strong acid.

10. The composition of claim 1, wherein said composition gives a spin bowl compatibility test result of at least about 90%.

11. A structure used in microlithographic processes, said structure comprising:

a substrate; and

a layer on said substrate, said layer formed from a composition comprising a polymer dissolved or dispersed in a solvent system, said polymer comprising recurring monomers having the formula



(I)

wherein:

each R is individually selected from the group consisting of hydrogen and alkyls; and

each R^1 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

12. The structure of claim 11, said structure further comprising an anti-reflective coating intermediate said substrate and said layer.

13. The structure of claim 11, said structure further comprising a photoresist adjacent said layer.

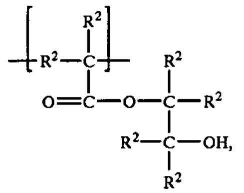
14. The structure of claim 12, said structure further comprising a photoresist adjacent said layer.

15. The structure of claim 11, wherein said substrate is selected from the group consisting of Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

16. The structure of claim 11, said polymer further comprising recurring monomers having an alcohol functionality.

17. The structure of claim 16, said polymer comprising recurring monomers having the formula

(II)



wherein each R^2 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

18. The structure of claim 11, said composition further comprising a cross-linking agent.

19. The structure of claim 18, wherein said cross-linking agent is selected from the group consisting of aminoplast cross-linking agents.

20. The structure of claim 11, said composition further comprising an acid.

21. The structure of claim 20, wherein said composition comprises a weak acid and a strong acid.

22. The structure of claim 11, wherein said layer gives a spin bowl compatibility test result of at least about 90%.

23. The structure of claim 11, wherein said layer has a thickness of less than about 2,150 Å.

24. The structure of claim 13, wherein said photoresist has a thickness of less than about 200 nm.

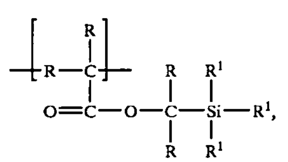
25. The structure of claim 14, wherein said photoresist has a thickness of less than about 200 nm.

26. A method of forming a structure for use in microlithographic processes, said method comprising the steps of:

providing a substrate; and

forming a layer of a composition on the substrate, said composition comprising a polymer dissolved or dispersed in a solvent system, said polymer comprising recurring monomers having the formula

(I)



wherein:

each R is individually selected from the group consisting of hydrogen and alkyls; and

each R^1 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

27. The method of claim 26, further including the step of applying an anti-reflective coating to said substrate and wherein said layer forming step comprises applying the layer to said anti-reflective coating.

28. The method of claim 26, further including the step of applying a photoresist to said layer.

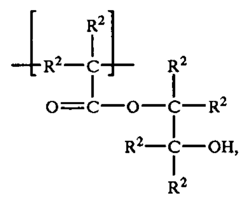
29. The method of claim 27, further including the step of applying a photoresist to said layer.

30. The method of claim 26, wherein said substrate is selected from the group consisting of Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

31. The method of claim 26, said polymer further comprising recurring monomers having an alcohol functionality.

32. The method of claim 31, said polymer comprising recurring monomers having the formula

(II)



wherein each R^2 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

33. The method of claim 26, said composition further comprising a cross-linking agent.

34. The method of claim 33, wherein said cross-linking agent is selected from the group consisting of aminoplast cross-linking agents.

35. The method of claim 26, said composition further comprising an acid.

36. The method of claim 35, wherein said composition comprises a weak acid and a strong acid.

37. The method of claim 26, wherein said layer gives a spin bowl compatibility test result of at least about 90%.

38. The method of claim 26, further comprising the step of curing said layer, and wherein said cured layer has a thickness of less than about 2,150 Å.

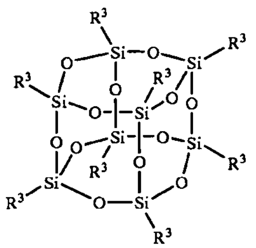
39. The method of claim 28, further including the step of drying said photoresist, wherein said dried photoresist has a thickness of less than about 200 nm.

40. The method of claim 29, further including the step of drying said photoresist, wherein said dried photoresist has a thickness of less than about 200 nm.

41. In a composition for use in microlithographic processes, wherein the composition comprises a constituent dissolved or dispersed in a solvent system, said constituent being selected from the group consisting of polymers, compounds, and mixtures thereof, the improvement being that said polymer includes recurring monomers comprising a polyhedral oligomeric silsesquioxane and that said compound comprises a polyhedral oligomeric silsesquioxane.

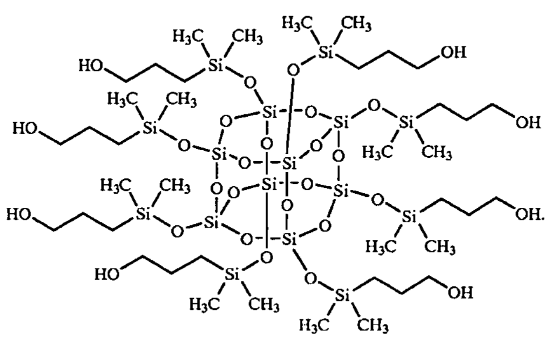
42. The composition of claim 41, wherein said constituent has the formula

(III)

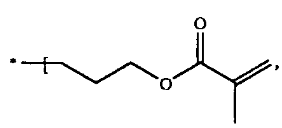


wherein each R^3 is individually selected from the group consisting of hydrogen, alkyls, aryls, hydroxypropyldimethylsilyloxy, and olefinic moieties.

43. The composition of claim 42, wherein said constituent is a compound having the formula



44. The composition of claim 42, wherein at least one R^3 is

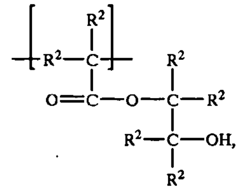


where "*" designates Si on (III).

45. The composition of claim 41, said polymer further comprising recurring monomers having an alcohol functionality.

46. The composition of claim 45, said polymer comprising recurring monomers having the formula

(IV)



wherein each R^2 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

47. The composition of claim 46, wherein the molar ratio of polyhedral oligomeric silsesquioxane to (IV) is from about 15:85 to about 30:70.

48. The composition of claim 41, said composition further comprising an ingredient selected from the group consisting of cross-linking agents, catalysts, and mixtures thereof.

49. The composition of claim 48, wherein said ingredient is a cross-linking agent selected from the group consisting of aminoplast cross-linking agents.

50. The composition of claim 48, wherein said composition comprises a catalyst.

51. The composition of claim 50, wherein said composition comprises a weak acid and a strong acid.

52. The composition of claim 41, wherein said composition gives a spin bowl compatibility test result of at least about 90%.

53. A structure used in microlithographic processes, said structure comprising:

a substrate; and

a layer on said substrate, said layer formed from a composition comprising a constituent dissolved or dispersed in a solvent system, said constituent being selected from the group consisting of polymers, compounds, and mixtures thereof, the improvement being that said polymer includes recurring monomers comprising a polyhedral oligomeric silsesquioxane and said compound comprises a polyhedral oligomeric silsesquioxane.

54. The structure of claim 53, said structure further comprising an anti-reflective coating intermediate said substrate and said layer.

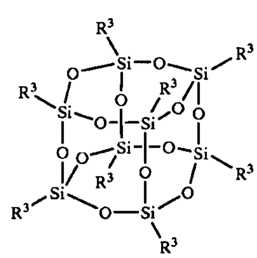
55. The structure of claim 53, said structure further comprising a photoresist adjacent said layer.

56. The structure of claim 54, said structure further comprising a photoresist adjacent said layer.

57. The structure of claim 53, wherein said substrate is selected from the group consisting of Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

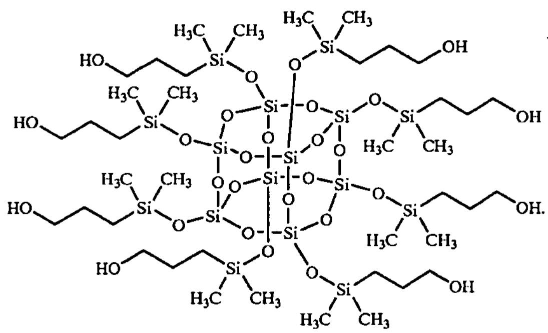
58. The structure of claim 53, wherein said constituent has the formula

(III)

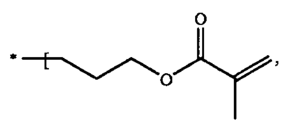


wherein each R^3 is individually selected from the group consisting of hydrogen, alkyls, aryls, hydroxypropyldimethylsilyloxy, and olefinic moieties.

59. The structure of claim 58, wherein said constituent is a compound having the formula



60. The structure of claim 58, wherein at least one R^3 is

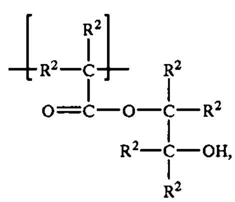


where "*" designates Si on (III).

61. The structure of claim 53, said polymer further comprising recurring monomers having an alcohol functionality.

62. The structure of claim 61, said polymer comprising recurring monomers having the formula

(II)



wherein each R^2 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

63. The structure of claim 53, said composition further comprising an ingredient selected from the group consisting of cross-linking agents, catalysts, and mixtures thereof.

64. The structure of claim 63, wherein said ingredient is a cross-linking agent selected from the group consisting of aminoplast cross-linking agents.

65. The structure of claim 63, wherein said composition comprises a catalyst.

66. The structure of claim 65, wherein said composition comprises a weak acid and a strong acid.

67. The structure of claim 53, wherein said layer gives a spin bowl compatibility test result of at least about 90%.

68. The structure of claim 53, wherein said layer has a thickness of less than about 2,150 Å.

69. The structure of claim 55, wherein said photoresist has a thickness of less than about 200 nm.

70. The structure of claim 56, wherein said photoresist has a thickness of less than about 200 nm.

71. A method of forming a structure for use in microlithographic processes, said method comprising the steps of:

providing a substrate; and

forming a layer of a composition on the substrate, said composition comprising a constituent dissolved or dispersed in a solvent system, said constituent being selected from the group consisting of polymers, compounds, and mixtures thereof, the improvement being that said polymer includes recurring monomers comprising a polyhedral oligomeric silsesquioxane and that said compound comprises a polyhedral oligomeric silsesquioxane.

72. The method of claim 71, further including the step of applying an anti-reflective coating to said substrate, and wherein said layer forming step comprises applying the layer to said anti-reflective coating.

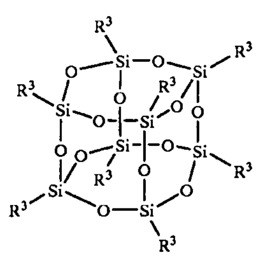
73. The method of claim 71, further including the step of applying a photoresist to said layer.

74. The method of claim 72, further including the step of applying a photoresist to said layer.

75. The method of claim 71, wherein said substrate is selected from the group consisting of Si substrates, SiO_2 substrates, Si_3N_4 substrates, SiO_2 on silicon substrates, Si_3N_4 on silicon substrates, glass substrates, quartz substrates, ceramic substrates, semiconductor substrates, and metal substrates.

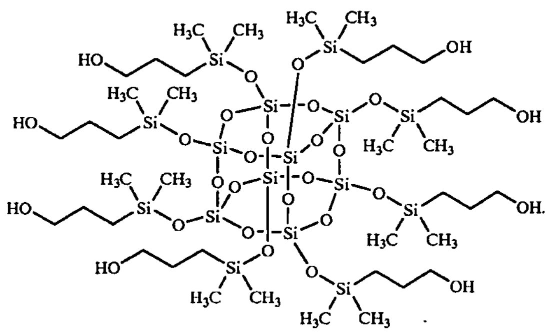
76. The method of claim 71, wherein said constituent has the formula

(III)

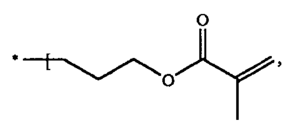


wherein each R^3 is individually selected from the group consisting of hydrogen, alkyls, aryls, hydroxypropyldimethylsilyloxy, and olefinic moieties.

77. The method of claim 76, wherein said constituent is a compound having the formula



78. The method of claim 76, wherein at least one R^3 is

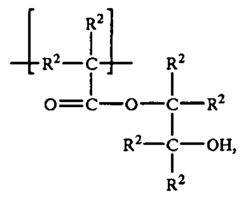


where "*" designates Si on (III).

79. The method of claim 71, said polymer further comprising recurring monomers having an alcohol functionality.

80. The method of claim 79, said polymer comprising recurring monomers having the formula

(II)



wherein each R^2 is individually selected from the group consisting of hydrogen, alkyls, and aryls.

81. The method of claim 71, said composition further comprising an ingredient selected from the group consisting of cross-linking agents, catalysts, and mixtures thereof.

82. The method of claim 81, wherein said ingredient is a cross-linking agent selected from the group consisting of aminoplast cross-linking agents.

83. The method of claim 81, wherein said composition comprises a catalyst.

84. The method of claim 83, wherein said composition comprises a weak acid and a strong acid.

85. The method of claim 71, wherein said layer gives a spin bowl compatibility test result of at least about 90%.

86. The method of claim 71, further comprising the step of curing said layer, and wherein said cured layer has a thickness of less than about 2,150 Å.

87. The method of claim 73, further including the step of drying said photoresist, and wherein said dried photoresist has a thickness of less than about 200 nm.

88. The method of claim 74, further including the step of drying said photoresist, and wherein said dried photoresist has a thickness of less than about 200 nm.

* * * * *